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Chemical Market Input/Output Analysis of Selected Chemical Substances to Assess Sources of Environmental Contamination: Task II. Biphenyl and Diphenyl Oxide

Syracuse Research Corp, N.Y.

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This report considers the sources of environmental contamination from biphenyl and diphenyl oxide. Biphenyl is manufactured in commercial quantities for use in dye carriers, heat transfer fluids, derivatives such as PCB's and alkylated biphenyls, and fruit fungicides. Diphenyl oxide is manufactured in commercial quantities for use in dye carriers, heat transfer fluids, derivatives such as butylchlorodiphenyl oxide, decabromodiphenyl oxide, surfactants, and perfumes and soaps. Thus, this report concentrates on the commercial production and use of biphenyl and diphenyl oxide. Standards established by the Occupational Safety and Health Administration have controlled the occupational exposure to biphenyl and diphenyl oxide; however, large quantities of these chemicals are released to the external environment, particularly to waste treatment facilities which may utilize chlorine disinfection. Laboratory studies indicate that the biphenyl nucleus can undergo chlorination to various chlorobiphenyl isomers during treatment chlorine disinfection.

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FINAL REPORT

CHEMICAL MARKET INPUT/OUTPUT ANALYSIS OF SELECTED CHEMICAL SUBSTANCES TO ASSESS SOURCES OF ENVIRONMENTAL CONTAMINATION TASK II: BIPHENYL AND DIPHENYL OXIDE

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I. Introduction

Occupational exposures to the compounds biphenyl and diphenyl oxide (phenyl ether) have been regulated by the Occupational Safety and Health Administration. The standards established by OSHA are directed at protecting workers who might be exposed occupationally to air vapors or particulates of biphenyl or diphenyl oxide. Until recently, however, little thought has been given to the amounts of biphenyl or diphenyl oxide that are released to the environment, and thus indirectly result in human exposure or environmental damage. Of additional concern are reports which have suggested that various PCB (polychlorinated biphenyl) isomers are formed when sewage, which contains biphenyl, is discharged to waste treatment plants utilizing chlorine for disinfection and deodorization (Carlson et al., 1975; Gaffney, 1974, 1976; Johnsen, 1975). Biphenyl and diphenyl oxide have also been shown to bioconcentrate several hundred times in fish and, therefore, small concentrates in water may result in significant concentrations in fish. This report considers environmental sources of biphenyl and diphenyl oxide and estimations of the amounts which may be exposed to the environment.

II. Historical Development and Future Outlook

A. Historical Development

1. Biphenyl

Biphenyl (diphenyl; phenylbenzene), $(C_6H_5)_2$, was first reported in 1862 by Fittig, who prepared it by the action of metallic sodium on bromobenzene. Berthelot prepared biphenyl in 1867 by passing benzene vapors through a red hot tube. In 1875, Büchner found biphenyl in high-boiling fractions from coal-tar distillation (Poffenberger, 1950).

In 1927, Theodore Swann of the Federal Phosphorus Co. was asked to supply biphenyl in commercial quantities for use as a heat transfer fluid in the refining of lubricating oils. He set up a pilot plant for this purpose. Soon after, the chlorination of biphenyl assumed commercial importance when the Swann Corp. developed the "Aroclor" series of PCB's (polychlorinated biphenyls); however, Monsanto took over the PCB production in the early 1930's. About that time, Dow Chemical Co. entered the commercial biphenyl field with Dowtherm® A, a eutectic mixture of biphenyl and diphenyl oxide for use in heat transfer. Historically, the two principal manufacturers of biphenyl have been the Monsanto Co. and the Dow Chemical Co. (Versar, 1976; Poffenberger, 1965).

The earliest commercial reactors were vessels holding a bath of molten lead at 750°C, through which benzene vapors were bubbled (Scott, 1933; Durgin and Jenkins, 1933). Later reactors used electrical resistance heaters to raise the temperatures above 650°C. The major technical problem was the tendency of benzene to decompose at very high temperatures to give carbon and heavy tar deposits which clogged the heat exchange surfaces. Practically all of the patents covering the manufacture of biphenyl have been proposed as solutions to this problem.

Patents have also been issued which identify biphenyl as a major by-product of phenol produced by the partial oxidation of benzene (Porter, 1946; Dundee, 1964). Biphenyl appeared on the U.S. market in 1964 which was refined from this process (Poffenberger, 1965). However, biphenyl currently produced by this method has little commercial importance due to the limited capacity of phenol production via partial oxidation of benzene.

In the late 1960's the commercial potential of recovering a biphenyl by-product formed when toluene is hydrodealkylated to benzene was realized. Today, the biphenyl obtained from the dealkylated toluene by-product is the most important commercial source of biphenyl. This apparently occurred due to large available quantities of the low-cost by-product and a sharp demand for biphenyl dye carriers. Approximately 70% of the current annual biphenyl production of 85 million pounds is obtained by refining the dealkylated toluene by-product (SRC estimation). The remaining 30% of the biphenyl production is produced by Monsanto's process of thermally reacting benzene vapors.

The earliest uses of biphenyl involved heat transfer agents and synthesis to PCB's. During the late 1940's, biphenyl began to be used as a mild fungicide when coated on individual fruit wrappers, although the patent describing this use was dated somewhat earlier (Mispley and Barber, 1940). More recently, biphenyl has been impregnated onto paper pads used in closed fruit packages. These fungicidal uses still exist today, but at a level which has slowly decreased due to better transportation and refrigeration systems.

In the 1960's, biphenyl found use as a dye carrier for disperse dye applications to polyester fibers. The use of biphenyl dye carriers has accelerated so greatly in the past six years that this use represents the largest

single application of biphenyl at present, consuming nearly 60% of the annual biphenyl production of 85 million pounds (SRC estimation). Large quantities of biphenyl, nearly 21 million pounds annually, are still being used for PCB manufacture; however, present legislation to eliminate PCB production will eliminate this use of biphenyl. Several million pounds of biphenyl are annually destined for heat transfer fluids. Since 1970, alkylated biphenyls have become commercially important, especially isopropylbiphenyl. Approximately 10 million pounds of isopropylbiphenyl are annually produced, at present, for applications in carbonless paper.

Commercial production of flame retardant PBB's (polybrominated biphenyls), which began in 1970, was thought to have been terminated in November, 1974, a year after PBB's were mistakenly added to cattle feed in Michigan (Mumma and Wallace, 1975). However, decabromo- and octabromobiphenyl were commercially produced in 1975 and 1976 for export purposes (Neufeld et al., 1977). In 1976, about 130 thousand pounds of biphenyl were consumed in the production of these two PBB products.

2. Diphenyl Oxide

Dr. Herbert H. Dow carried out experiments with diphenyl oxide (phenyl ether, diphenyl ether, phenoxybenzene, DPO) in 1925-1926, using it as a heat transfer fluid in a steam power process. These experiments eventually led to the development of Dowtherm® A, a eutectic heat transfer mixture of 73.5% diphenyl oxide and 26.5% biphenyl, in the early 1930's. Dowtherm® A has been a widely-used heat transfer fluid since that time.

The original American patents describing diphenyl oxide production were assigned to the Dow Chemical Co. The first patent (Hale, 1930) described the production of diphenyl oxide as heating equimolar amounts of chlorobenzene and aqueous base, such as Na_2CO_3 or NaOH, under pressure with copper catalysts. The second patent (Hale and Britton, 1933) refers to the Dow process of phenol production from chlorobenzene and aqueous base. In this process, diphenyl oxide is formed as a by-product. Historically, nearly all of the diphenyl oxide produced in the U.S. has been obtained from the by-product from Dow's chlorobenzene-phenol process. However, Monsanto has recently entered the commercial diphenyl oxide market. A new Monsanto unit, completed in late 1975, produces high-purity diphenyl oxide in a one step process which involves reacting phenol in the presence of a catalyst.

The only commercially important early use of diphenyl oxide, other than for Dowtherm® A heat transfer fluid, was for applications with perfumes and soaps. Diphenyl oxide has a characteristic geranium odor. Use in perfumes and soaps is still important, with roughly 100,000 pounds annually consumed. Historically, most of diphenyl oxide produced has been used to formulate Dowtherm® A. Roughly two-thirds of the estimated 6 million pounds of diphenyl oxide produced in 1975 was used in Dowtherm® A (SRC estimation).

Other commercially important current uses of diphenyl oxide include Dowfax® (alkylated sulfonated derivatives) surface-active agents, decabromodiphenyl oxide flame retardants, diphenyl oxide dye carriers, and butylchlorodiphenyl oxide capacitor fluid. Dowfax® production started in the early 1960's and decabromodiphenyl oxide and diphenyl oxide dye carriers started in the 1970's. Butylchlorodiphenyl oxide is discussed in Future Outlook - Diphenyl Oxide.

Several diphenyl oxide derivatives, chloromethyl diphenyl oxides, and methoxymethyl diphenyl oxide, have minor commercial uses in polymer and resin production.

B. Future Outlook

1. Biphenyl

The sizeable increase in biphenyl production from 1970 to the present is primarily due to the dye carrier use of biphenyl in polyester dyeing. Future increases in production may, therefore, be aligned with increases in the polyester market. Several industry spokesmen are projecting an 85% increase in the polyester market by 1980 and a 170% increase by 1985. Biphenyl, however, is only one of perhaps eight to ten commercially important dye carriers used in polyester dyeing. After consulting with industry spokesmen, it is estimated (SRC estimation) that biphenyl dye carriers make up approximately 25-30% of the total dye carrier market at present. The total dye carrier market is expected to increase by 47% by 1980. This 47% figure is smaller than the 85% polyester growth figure because technological improvements in dyeing techniques should decrease the amount of dye carrier which is required.

If biphenyl maintains 25-30% of the dye carrier market, an additional 20-25 million pounds of biphenyl will be used for dyeing by 1980. Present biphenyl consumption in dye carriers is estimated at 50 million lbs. annually (SRC estimation).

Increased biphenyl consumption is also projected for heat transfer fluids and alkylated biphenyls. Dow has announced an expansion of their Dowtherm® A units, to be completed by 1978 (Anon., 1976 a). In early 1976, Monsanto began commercial production of Therminol VP-1 heat transfer fluid, which will compete

with Dow's Dowtherm® A. Therminol VP-1 and Dowtherm® A have identical chemical compositions. Isopropylbiphenyl, used in carbonless paper, and methylbiphenyl, used as a dye carrier, are also expected to increase output by 1980. A guess would project that nearly 10 million additional pounds of biphenyl will be used for heat transfer and alkylation by 1980 (SRC estimation).

The projected phase-out of PCB's which is required by section 6e of the Toxic Substances Control Act (PL 94-469) would decrease the needed biphenyl production by nearly 21 million pounds annually. However, alternatives to PCB's may include another biphenyl derivative. Effects to the biphenyl market by the PCB phase-out cannot be ascertained at this time.

2. Diphenyl Oxide

There will be large increases in the production of diphenyl oxide by 1980. Until the end of 1975, the only commercial quantities of diphenyl oxide were obtained from Dow's chlorobenzene-phenol process as a by-product. This amounted to approximately 6 million pounds annually (SRC estimation). However, at the end of 1975, Monsanto began commercial production of diphenyl oxide for use in Therminol VP-1 heat transfer fluid. Also, Dow has announced a $37 million expansion of their chlorobenzene complex to be completed in 1978. This will include expansion of diphenyl oxide production, primarily for use in butylchlorodiphenyl oxide, but also for Dowtherm® A and decabromodiphenyl oxide (Anon., 1976 a). An estimated $10 million of this expansion had been completed by April, 1976.

The primary reason for Dow's diphenyl oxide expansion appears to be synthesis of butylchlorodiphenyl oxide. Dow is hoping that butylchlorodiphenyl oxide will be widely accepted as a PCB replacement in capacitors. McGraw-Edison, a capacitor manufacturer, has totally converted to the use of this Dow product in

1976, making a reality of commercial production. Dow says it hopes to have production capacity in excess of 5 million lbs/year of butylchlorodiphenyl oxide by the end of 1976 (Anon., 1976b). If this 5 million lb figure proves correct, then diphenyl oxide production in the U.S. will have doubled in a year's time. The degree of diphenyl oxide expansion in the future may be determined by industry's acceptance of butylchlorodiphenyl oxide as a PCB substitute. It should be noted, however, that other companies are developing and evaluating PCB substitutes different from butylchlorodiphenyl oxide.

III. Market Input/Output Data

A. Production

Table III-1 lists the domestic producers of refined biphenyl with their respective production sites, years, and capacities. Also listed in Table III-1 are the petrochemical companies who commercially supply unrefined biphenyl feed stock (by-product from toluene dealkylation) to biphenyl refiners. Annual biphenyl production is shown in Figure III-1.

Two companies have stopped refined biphenyl production. First is Geneva Industries of Houston, Texas, who sold their biphenyl refinery to Pilot Industries in 1974. Second is Bethlehem Steel Corp. of Sparrows Point, Maryland, who terminated biphenyl refining in 1974.

The Dow Chemical Co. and Monsanto Industrial Chemicals Co. are the only domestic producers of diphenyl oxide. The Dow production site is located in Midland, Michigan, while Monsanto's site is located at their Chocolate Bayou facility in Alvin, Texas. Dow has been involved in the production of diphenyl oxide since the early 1930's. Monsanto began commercial production at the end of 1975.

Dow did not release their annual production volumes, as the information is considered confidential (Otis, 1976). However, before the current diphenyl oxide expansion, Dow obtained all of their diphenyl oxide as by-products from their chlorobenzene-phenol process. Capacity of this phenol process has been estimated at 48-70 million pounds annually (SRI, 1975 a, 1976). Since approximately 0.1 pound of diphenyl oxide is formed for every 1.0 pound of phenol formed (Hahn, 1970), the annual diphenyl oxide output would be 4.8 to 7.0 million pounds; and, therefore, 6 million pounds may be a good estimate of the annual

Table III-1. United States Biphenyl Producers

Refined Biphenyl Producers - 1976

Producer	Production Site	Years	Estimated Capacity (x 10^6 lb/yr)
1. Chemol, Inc.	Greensboro, NC	1972 - Present	5
2. CPS Chemical Co., Div. of Chemistry & Pollution Sciences	Old Bridge, NJ	-	< 1
3. Dow Chemical Co.	Bay City, MI	1971 - Present	10 - 20
4. East Coast Chemical Co.	Cedar Grove, NJ	1974 - Present	1 - 4
5. Monsanto Industrial Chemicals	Anniston, AL	1933 - Present	45
6. Pilot Industries	Houston, TX	1974 - Present	15 - 20
7. Sun Oil of Penn. (Suntide)	Corpus Christi, TX	1970 - Present	10 - 20
8. Sybron Corp., Tanatex Chemicals Div.	Lyndhurst, NJ	1971 - Present	10

Biphenyl Feed Stock Producers - Commercially Available Product

1. Coastal States Gas Producing Co.	Corpus Christi, TX
2. Cosden Oil and Chemical Co.	Big Spring, TX
3. Dow Chemical Co.	Bay City, MI
4. Gulf Oil Corp.	Philadelphia, PA

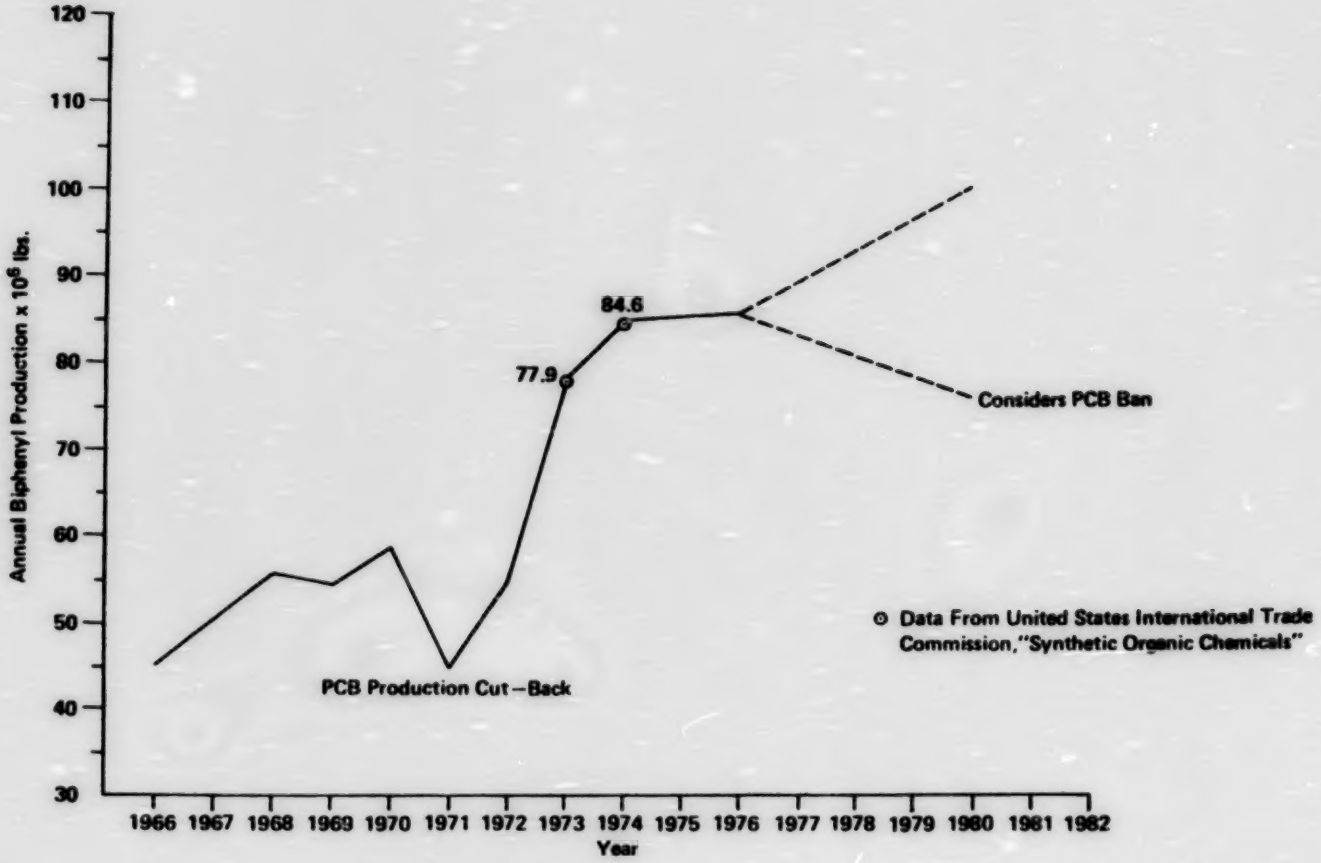


Figure III-1. Annual Biphenyl Production (SRC Estimations)

capacity. Of course, that figure is somewhat higher currently, depending upon how much of the chlorobenzene expansion has been completed.

The production capacity of Monsanto's facility for diphenyl oxide is considered proprietary and has, therefore, not been obtained. Monsanto produces diphenyl oxide by reacting phenol with catalyst.

B. Importation

Prior to 1974, there is no record in the literature of any importation of biphenyl or diphenyl oxide. However, the 1974 edition of "Imports of Benzenoid Chemicals and Products" (United States International Trade Commission) lists the following imports:

Biphenyl	10,758 pounds
Phenyl Ether (Diphenyl Oxide)	43,201 pounds

It should be noted that this reference source includes only surveys conducted at the major ports of entry. The above quantities are relatively insignificant when compared to the total biphenyl and diphenyl oxide consumption in the United States; they represent less than 1% of the yearly consumption.

"Imports of Benzenoid Chemicals and Products" (1967-1974 editions) also list imports of unspecified "textile assistants" ranging from 1.4 to 4.7 million pounds annually. The chemical ingredients of these textile assistants have not been determined by SRC. It is possible that some of these textile assistants are biphenyl dye carriers, although it would be surprising if more than one million pounds of biphenyl are imported via this route.

It is also possible that quantities of biphenyl and diphenyl oxide are imported as heat transfer fluids with compositions identical to Dowtherm® A. These heat transfer fluids, made overseas, are listed in Section V-B-1; quantities which may be imported were not obtainable.

C. Exportation

No figures revealing export quantities of biphenyl or diphenyl oxide were available. After consulting with industry spokesmen, it is believed that small quantities of biphenyl dye carriers are exported to Canada and Mexico. Also, biphenyl fungicide pads are used for overseas shipments of fruit, but this quantity is less than a million pounds. Overseas exportation, in bulk quantities, appears to be virtually unknown.

D. Use Patterns

Figure III-2 and Figure III-3 diagram the 1976 uses of biphenyl and 1975 uses of diphenyl oxide, respectively. Quantities used in each application are included where known or estimated.

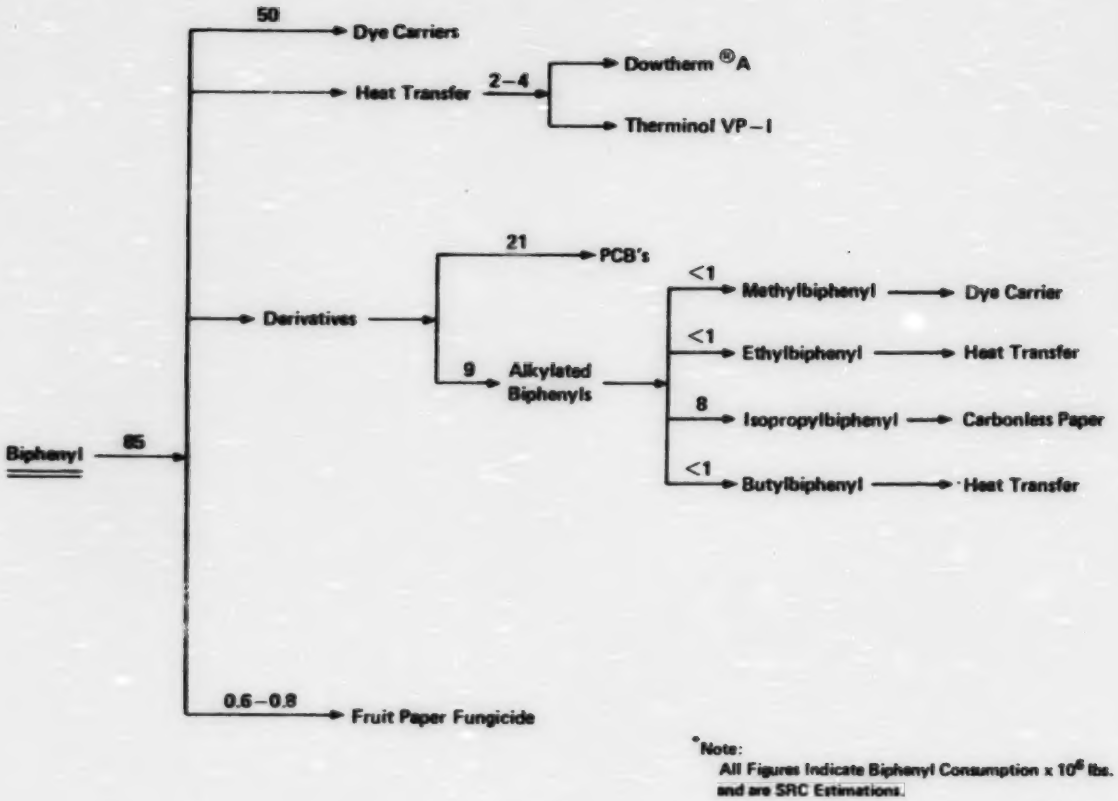


Figure III-2. 1976 Annual Biphenyl Use in the United States

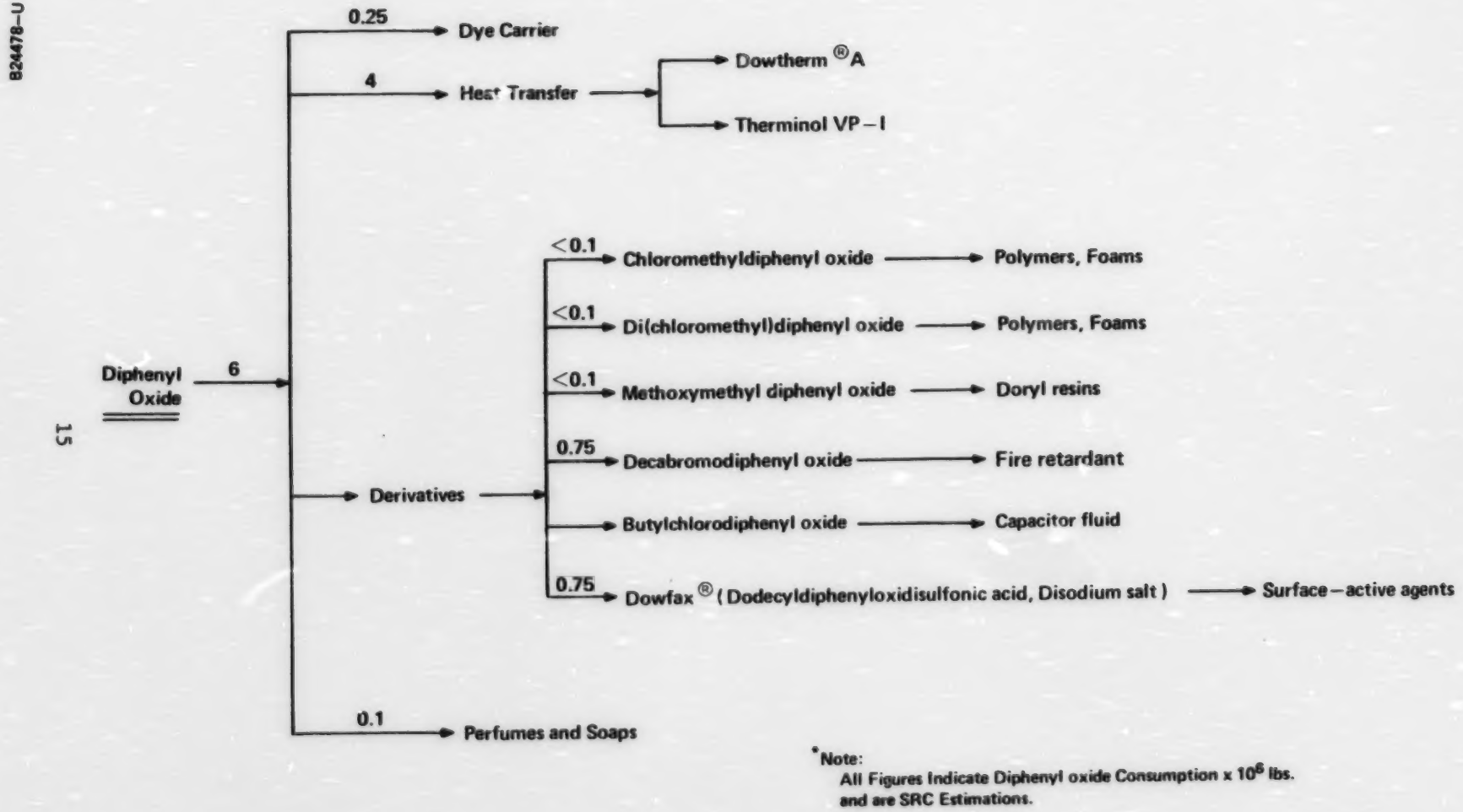


Figure III-3. Domestic Diphenyl Oxide Use in 1975

IV. General Manufacturing and Production Technology

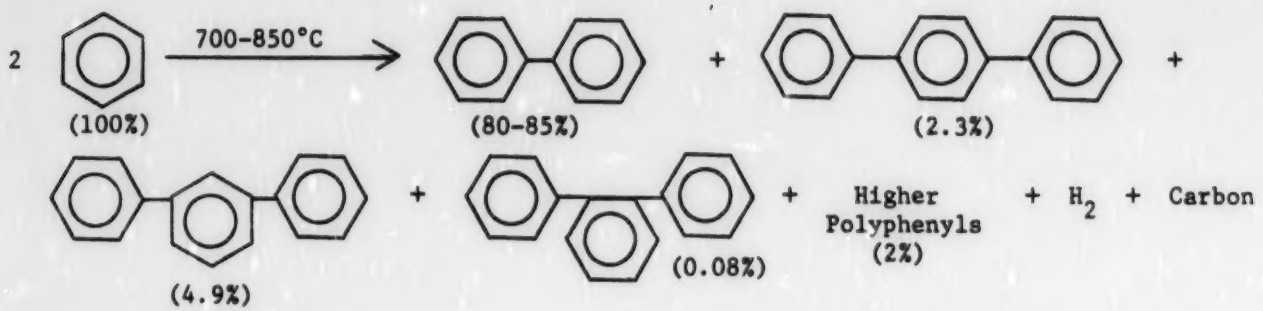
A. Biphenyl

1. Thermal Dehydrogenation of Benzene

Monsanto Industrials Chemicals Co., located in Anniston, Alabama, is the only current biphenyl producer to use the thermal dehydrogenation of benzene process. Both Monsanto and Dow began using the process in the 1930's; however, Dow termination their process in 1968 in favor of biphenyl production from dealkylated toluene.

a. Manufacture

The chemistry involved in the thermal dehydrogenation of benzene is shown in the following reaction:



At temperatures of 700-850°C, benzene reacts by a homogeneous gas-phase reaction (in which a benzene molecule joins with another benzene molecule or with a polyphenyl molecule, liberating hydrogen and forming biphenyl or higher polyphenyls) or by a heterogenous gas-solid phase reaction, giving carbon and hydrogen. Most process development work has been directed to repressing the second reaction, which is catalyzed by metals, particularly iron, copper, and nickel (Poffenberger, 1965).

Figure IV-1 illustrates the typical process method of biphenyl production from thermal dehydrogenation of benzene. The raw material benzene and recycled benzene are vaporized and heated to about 600°C and then injected into a thermal reactor at 1-2 atm. pressure. The reactor raises the temperature to 700-850°C, the time of exposure to the higher temperatures being on the order of one second. Under these conditions, a well-designed thermal reactor yields a condensed product containing 12-15% by weight of biphenyl, terphenyl, and polyphenyls corresponding to approximately 20% by weight of the biphenyl, and the remainder as unreacted benzene. The yield of biphenyl, based on benzene consumed, should be 80-85% of theory. The yield of biphenyl plus terphenyl and other polyphenyls should be 90-95% of theory. At a 15% conversion per pass, the yield of biphenyl is 0.80 lb and that of terphenyl, etc. is 0.12 lb per pound of consumed benzene. The mechanical loss of benzene is 0.02-0.04 lb per pound of consumed benzene (Poffenberger, 1950, 1965).

The product from the reactor is condensed in a heat exchange system and then distilled to drive off the benzene which is recycled. The biphenyl-rich still residues are then vacuum distilled to separate the biphenyl from the terphenyls, etc. Benzene in the noncondensable gas (mostly hydrogen) vented from the heat exchange system is recovered either by compression or activated charcoal adsorbers. All of the benzene is passed through the heat exchangers to raise the benzene temperature and to cool the reactor products' temperature (Sanders and Slocombe, 1955; Poffenberger, 1950, 1965).

Heat is generated in the thermal reactor by means of electrical resistance elements. At temperatures above 650°C, benzene has a tendency to decompose to give carbon and heavy tar deposits which coat heat exchange surfaces.

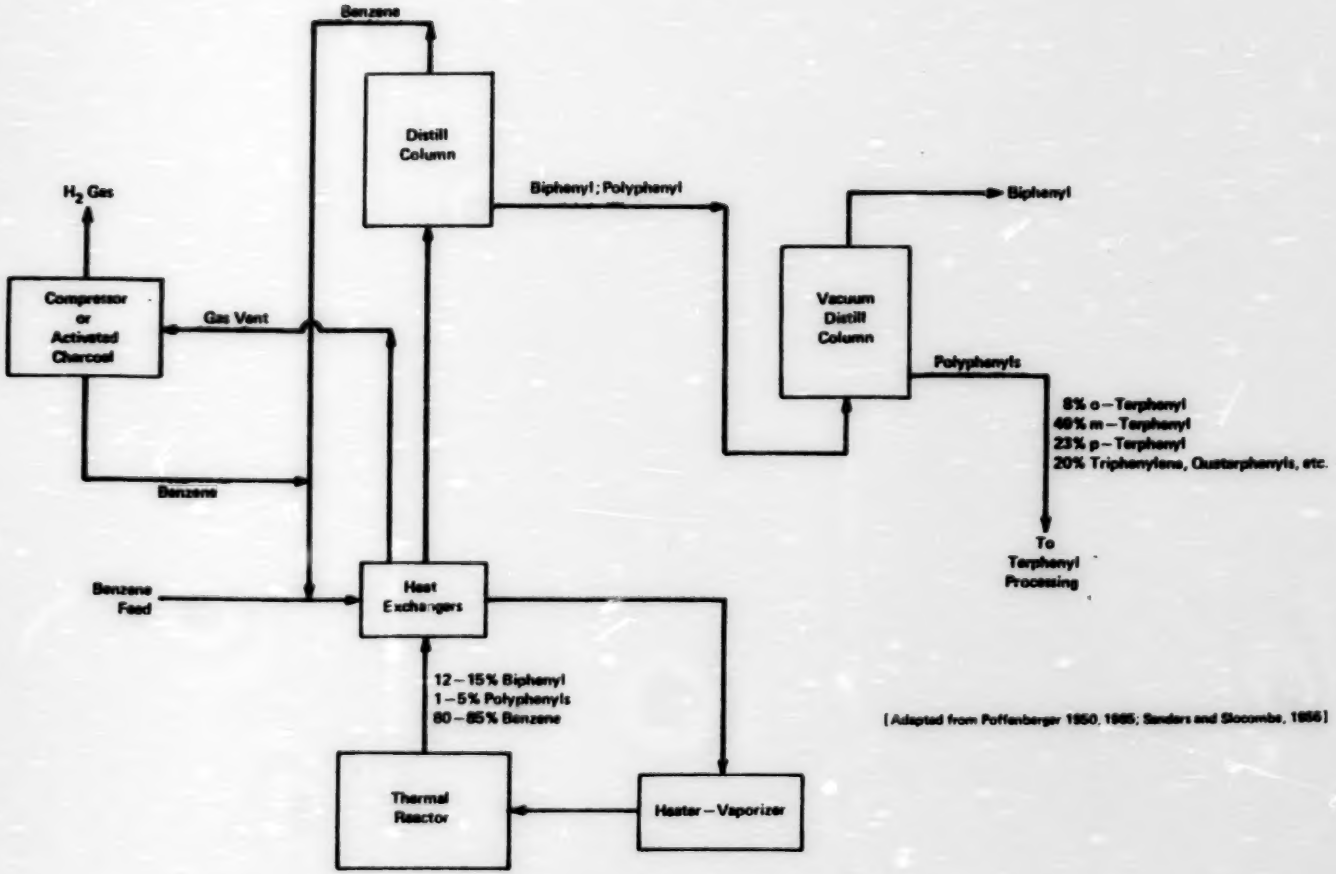


Figure IV-1. Biphenyl From Thermal Dehydrogenation of Benzene

Metal surfaces made of iron, nickel, or copper catalyze this carbon formation; therefore, metal surfaces are coated with carbide, nitride, or oxide to reduce the catalytic effects (Prutton, 1940; Moose and Pritchard, 1934).

The following shipping information is available (Monsanto Technical Bulletin 1C/FF-29):

Shipping Classification (U.S.):	Diphenyl (phenyl benzene)
Labelling:	Product label
Standard Containers:	50 lb net multiwall bags 260 lb net fibre drums Tank trucks Tank cars

b. Production Volumes

Monsanto is the only domestic biphenyl producer currently utilizing thermal dehydrogenation of benzene. Most of the biphenyl presently made by Monsanto is captively used to produce PCB's (SRC estimation). Approximately 21 million pounds of biphenyl are required for the annual PCB production of 40 million pounds. Additionally, slightly less than one million pounds of biphenyl may be supplied by Monsanto for fungicidal purposes (SRC estimation). Monsanto has also just begun production of a heat transfer fluid called Therminol VP-1, which is an eutectic mixture of 26.5% biphenyl and 73.5% diphenyl oxide. Several million pounds of biphenyl may be required for annual production of Therminol VP-1.

The capacity of Monsanto's Anniston, Alabama biphenyl unit is probably twice that of current utilization. In 1970, Monsanto produced 85 million lbs of PCB's (Versar, 1976), which would require approximately 44 million pounds of biphenyl. After 1970, Monsanto restricted PCB sales to closed system uses; hence, production was cut approximately in half.

c. Economics

The current (1976) selling price of Monsanto's biphenyl is $0.36/lb; however, most is captively used in synthesis of PCB's.

To estimate the raw material cost to produce biphenyl via thermal dehydrogenation of benzene, the yields previously described have been assumed: 1 lb of consumed benzene yields 0.80 lb biphenyl and 0.12 lb terphenyl, etc. Also, the current selling price of benzene is $0.80/gallon or $0.11/lb.

Therefore, one pound of biphenyl consumes $0.136 worth of benzene raw material. Additional costs must be added for equipment, labor, insurance, transportation, etc.

d. Environmental Management

The only wastes from the process are the crude still pot residues, which will be high molecular weight hydrocarbons, tars, and carbon. It is very likely that a small amount of biphenyl will be present in these residues; however, a chemical composition breakdown of the still pot residues was not available. Also, the environmental fate of these residues was not determined, but it is suspected that the residues are burned for fuel purposes or used in coking operations. Due to the nature of the process, large amounts of biphenyl cannot be released to the environment and any amounts which may be released are very much smaller than amounts released by the dyeing industry.

e. Alternative Biphenyl

The advantage of Monsanto biphenyl is the purity, a very high-grade product compared to biphenyl normally produced from dealkylation of toluene. The disadvantage is price, $0.36/lb compared to $0.16-$0.25/lb for dealkylated toluene biphenyl. Since the lower-grade biphenyl is suitable for dye carrier application, Monsanto's biphenyl is not very competitive for this large quantity use.

2. By-Product From Dealkylation of Toluene

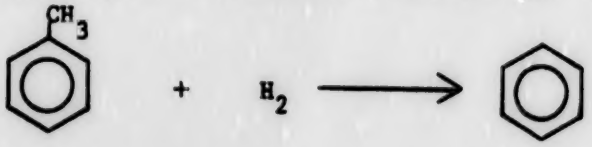
The companies listed below are all currently refining biphenyl from a by-product obtained when toluene is hydrodealkylated to benzene:

Chemol, Inc.	Greensboro, NC
Dow Chemical Co.	Bay City, MI
East Coast Chemical Co.	Cedar Grove, NJ
Pilot Industries	Houston, TX
Sun Oil of Penn.	Corpus Christi, TX
Sybron Corp., Tanatex Chemical Div.	Lyndhurst, NJ

Dow Chemical and Sun Oil generate their own by-product, while the other companies listed above purchase the by-product feedstock from one of the following petroleum companies: Coastal States Gas Producing Co. (Corpus Christi, TX), Cosden Oil and Chemical Co. (Big Spring, TX), Dow Chemical (Bay City, MI), or Gulf Oil Corp. (Philadelphia, PA).

a. Chemistry

Hydrodealkylation involves the removal of one or more alkyl groups from alkylbenzenes to produce high-grade benzene as the end product. The reactions are carried out either thermally or catalytically in the presence of excess hydrogen at elevated temperatures and pressures. When toluene is used as the starting material, the principal hydrodealkylation reaction leading to the selective product formation of benzene is:

(1)  (Doelp, 1966)

The types of reactions contributing most to the nonselective product formation are the following:

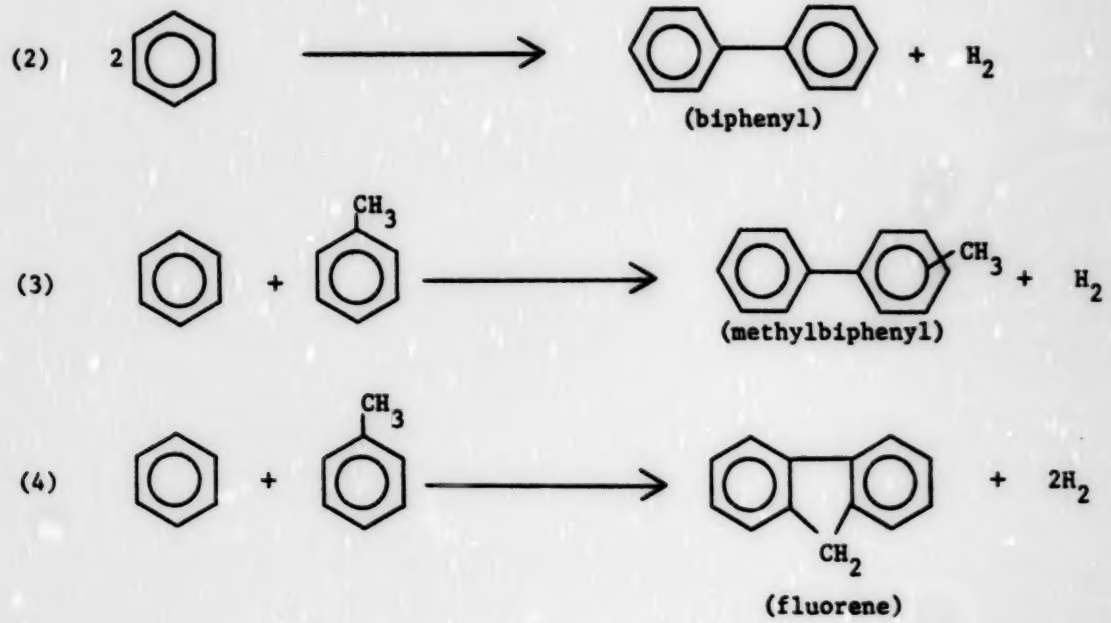


Figure IV-2 illustrates the general process for hydrodealkylating toluene to benzene. The various companies employ slightly different techniques to accomplish the basic operations; however, the overall processes are quite similar.

The toluene feed and hydrogen-rich gas are heated to an elevated temperature and pumped into a tubular reactor of 400 - 1000 psig pressure and 811 - 1033°F temperature. The hydrogen-to-toluene mole ratio is 4-12. This stoichiometric excess of hydrogen helps to suppress the non-selective reactions. Contact time in the reactor averages 20-80 seconds (Doelp, 1966). Catalysts are used in several processes.

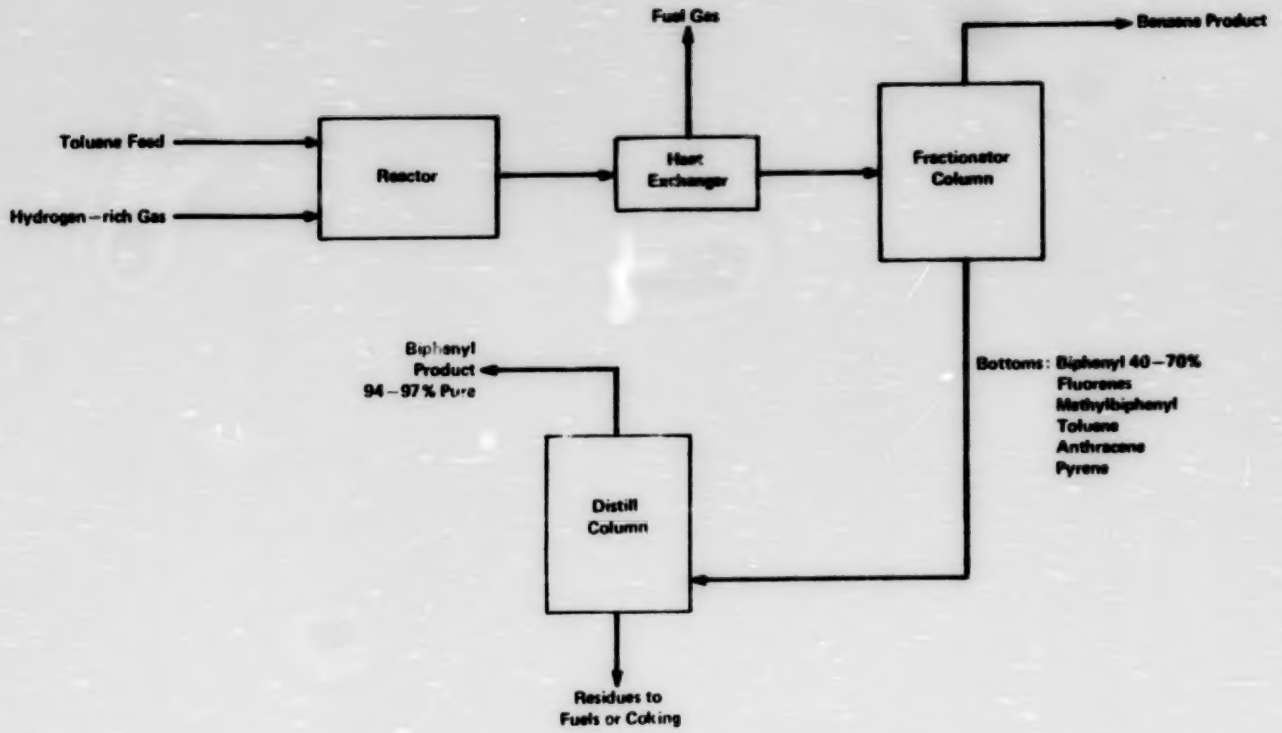


Figure IV-2. General Process for Hydrodealkylating Toluene to Benzene

The product from the reactor is condensed through heat exchangers and the fuel gas (hydrogen and methane) is vented off for fuel uses. Benzene is separated from the non-selective products by fractional distillation. The yield of benzene from toluene is greater than 95% of theoretical.

The bottoms residue from the benzene fractionator will vary slightly from company to company. However, an average composition for this residue would be (Earhart, 1976; Derrig, 1976; Doelp, 1966):

Biphenyl	50%
Toluene	15-20%
Fluorenes	10-15%
Methyl biphenyls	5%
Anthracene	3%
Pyrene	3%
Other Aromatic Hydrocarbons	9%

The weight of the bottoms residue is approximately 2% of the weight of toluene feed. Therefore, approximately one pound of biphenyl is formed for every 100 pounds of toluene which is dealkylated.

These bottoms from the benzene fractionator have two uses. Economically, the best use is to refine the biphenyl or sell the bottoms to biphenyl refiners (if the refined biphenyl can be sold). Otherwise, these bottoms are usually added to fuel oils and burned as fuels.

The biphenyl is refined from the other hydrocarbons in the benzene fractionator bottoms by distillation. A biphenyl product of 95-97% purity is commonly obtained, which is quite suitable for use in dye carriers. The residues from the biphenyl distillation are either added to fuels or used in coking operations.

Bulk shipments of biphenyl to customers is done via railway or truck tankers in a molten state (biphenyl melts at 69°C).

c. Production Volumes

Estimated capacities of the biphenyl refiners are listed in Table III-1, p. 10. Roughly 60 million pounds of refined biphenyl are currently being obtained from dealkylated toluene (SRC estimation). Ten years ago, the figure was very nearly zero. The sharp increase has come since 1970.

d. Environmental Management

The nature of this production method limits biphenyl release to the environment to virtually nothing. More biphenyl is probably spilled during loading of tankers than released in plant effluents (Earhart, 1976). Appendix B contains Material Safety and Handling Sheets.

e. Economics

The biphenyl by-products from toluene dealkylation have become available recently due to economic considerations concerning benzene. The price of benzene has risen from $0.22/gallon in 1970 to nearly $0.80/gallon in 1976. With the current price of toluene in the $0.55/gallon range, the profit potential of obtaining benzene by simply dealkylating toluene can be appreciated. Some of the dealkylation units idled or cut-back in 1970 are now running nearer to capacity and new units are being installed. This increase in dealkylation of toluene has resulted in a biphenyl by-product from which profits can be realized. Therefore, the biphenyl by-product has found use as fuel additives or as a refined product.

The biphenyl by-product can be sold to biphenyl refiners for $0.35 per gallon of which approximately 50% by weight is biphenyl (Derrig, 1976). The biphenyl content of the by-product would, therefore, have a selling value of about $0.085/lb. The refined biphenyl can be sold to dye carrier manufacturers

for $0.16-$0.25/lb., depending upon the purity. This would indicate that refined biphenyl obtained from dealkylation of toluene accounts for annual sales of $10-15 million. The quoted prices for this biphenyl in 1973 was $0.03-$0.07 less per pound than current prices.

A number of petrochemical companies produce a biphenyl by-product from dealkylating toluene, but do not refine the biphenyl and do not sell it to refiners. They use it only as an additive to fuel oils. These companies and the quantities of biphenyl put in fuel oils will be discussed in Section VII-A-1.

3. By-Product From Partial Oxidation of Benzene

CPS Chemical Co. of Old Bridge, NJ is currently refining small quantities of biphenyl from a by-product obtained when phenol is formed by partial oxidation of benzene. Production volumes of this refined biphenyl are much less than one million pounds annually.

a. Process Description

A vapor phase mixture of benzene and oxygen are passed through a tubular reactor of 0.5 - 2.0 atm. pressure and 600-800°F. Of the benzene which reacts, 43% yields phenol, 25% yields biphenyl, and the rest yields gaseous products (Porter, 1946). The biphenyl is obtained by distillation.

This process for the production of phenol is so minor a commercial method that it receives virtually no mention in the available literature.

B. Diphenyl Oxide

1. By-Product From Chlorobenzene-Phenol Process

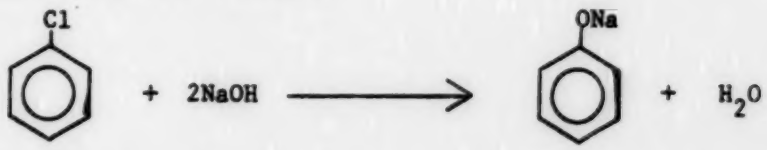
a. Manufacture

The Dow Chemical Co., plant site located in Midland, MI, produced diphenyl oxide as a by-product from their phenol production via chlorobenzene until the phenol operation was shut-down in 1975. This entire process is illustrated in Figure IV-3.

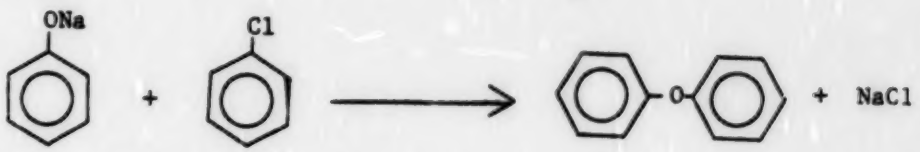
Brine undergoes electrolysis to produce hydrogen gas, chlorine gas, and caustic soda (NaOH). The chlorine is used to chlorinate benzene to monochlorobenzene. A one mole ratio of monochlorobenzene and a 2-2 1/2 mole ratio of a 10-15% aqueous caustic soda solution are then introduced into a high pressure pump along with a small percentage of diphenyl oxide. The diphenyl oxide is added to repress its own formation during the hydrolysis reaction. It should be noted that the quantity of diphenyl oxide produced as by-product can be partially controlled by the quantity of diphenyl oxide recycled to the high pressure pump. It provides a degree of flexibility to a process designed primarily for the production of phenol. Other materials added to the reactants in comparatively small quantities are anticorrosion agents (amines), emulsifiers (hydroxydiphenyl), and a catalyst (copper salts) (Faith et al., 1965).

The reactants are then pumped through a nickel-lined, counter-current heat exchanger which raises the reactants' temperature to 275-300°C. The flow is injected into a continuous-flow tubular reactor of 4000-5000 psi pressure and heated to 400°C. Contact time is usually 15-20 minutes at the 400°C temperature. The selective and non-selective reactions which occur in the reactor are the following:

(selective)



(non-selective)



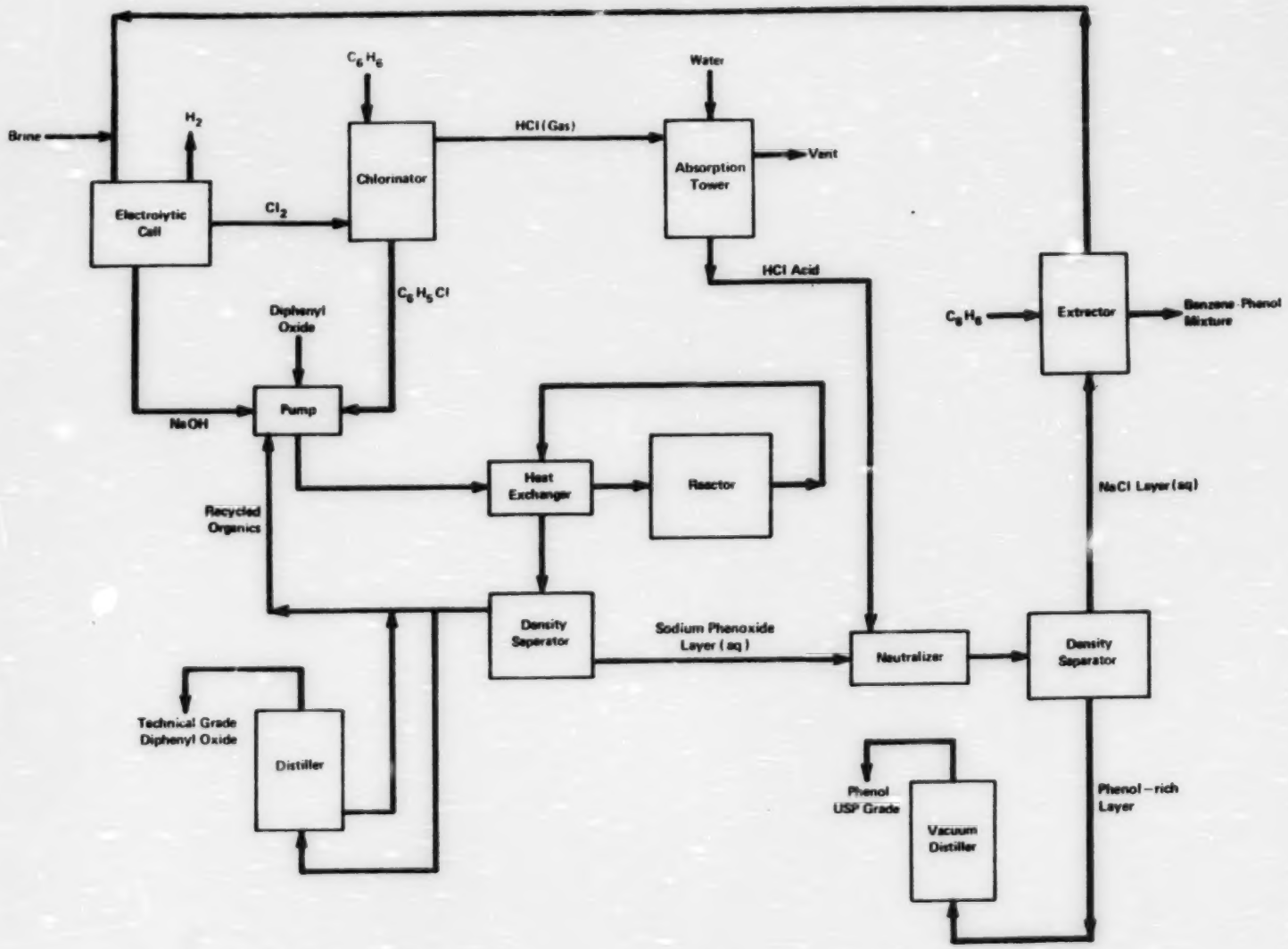


Figure IV-3. Diphenyl Oxide from Chlorobenzene - Phenol Process

When leaving the reactor, the reaction products are passed through the heat exchanger once again, to warm the incoming reactants and to cool the reaction products. The reaction products are then allowed to settle in a density separator. Two phases are obtained: (1) an aqueous sodium phenoxide phase, and (2) an oil phase consisting principally of diphenyl oxide and unreacted monochlorobenzene. The oil is distilled to produce diphenyl oxide and the monochlorobenzene is recycled to the reactor. The aqueous sodium phenoxide layer is passed to a neutralizer and treated with hydrochloric acid prepared from the HCl gas by-product from the chlorinator. The neutralization reaction which produces phenol is:

The product from the neutralizer is density separated to produce an aqueous NaCl layer and a phenol-rich layer. The phenol layer is distilled to obtain USP grade phenol. The NaCl layer is extracted with benzene to remove phenol content, and the NaCl solution is returned to the electrolytic cell. The phenol-benzene mixture is distilled to obtain high-purity phenol (Poffenberger, 1968; Faith et al., 1965).

The overall yield of phenol based on monochlorobenzene is 90-95% by weight. Conversion per pass through the reactor is 35-45% (Faith et al., 1965). Approximately 0.1 pound of diphenyl oxide is formed per pound of phenol formed (Hahn, 1970), but additional diphenyl oxide will be produced if it is not introduced into the high pressure pump to limit the non-selective reaction. Small amounts of ortho and para-phenylphenol are formed as by-products during the neutralization and are separated from the phenol-rich layer during

distillation. Ortho-phenylphenol is used as a dye carrier and as an active ingredient in Lysol® cleaner.

The diphenyl oxide obtained from the initial distillation of the oil-layer from the reactor is a "technical" grade diphenyl oxide. This technical grade can be purified to Dow's "perfume" grade diphenyl oxide. Purification can be done by crystallization from solution in methyl alcohol (Britton and Reed, 1933). The technical and perfume grades differ only slightly in odor, the distinction being apparent only to individuals trained in screening by olfactory response. Dow also offers an "industrial" grade diphenyl oxide. This industrial grade is intended for use as a dye carrier, and assays about 90% diphenyl oxide (Dow Form No. 11028872). The additional 10% makeup is primarily naphthalenes and methyl naphthalenes (also effective dye carriers).

b. Production Volumes

Production quantities of diphenyl oxide from the Dow facility are considered confidential information (Otis, 1976), and cannot be obtained. However, the now defunct (terminated in 1975) phenol capacity of Dow's chlorobenzene process had been estimated at 48-70 million pounds annually (SRI, 1975, 1976). Since approximately 0.1 lb of diphenyl oxide are formed per pound of phenol formed, the annual diphenyl oxide capacity could have been 4.8-7.0 million pounds. Therefore, up to 1975, the annual diphenyl oxide production from this process is estimated at 6 million pounds.

The Dow chlorobenzene and diphenyl oxide facilities at Midland, MI are currently undergoing revision and expansion to be completed in 1978. Ten million dollars of the total $37 million expenditure for this revision and expansion have been completed to date (Anon., 1976 a). Estimates of future diphenyl oxide capacities are not available.

c. Shipping

The technical and industrial grades of diphenyl oxide are shipped via tank cars and tank trucks in a molten state. Freezing point of the molten diphenyl oxide is approximately 80°F, so only minimal heating from steam coils is required to maintain a molten form. Size of the tankers can range from 4,000-10,000 gallon railway tankers to 5,000 gallon trucks. No extra-ordinary precautions are required during shipping.

Technical grade diphenyl oxide can also be shipped in black iron drums of 55 gallon capacity. Perfume grade diphenyl oxide is shipped in 55 gallon galvanized steel drums. These drums are equipped with dip pipes for convenient removal of the diphenyl oxide in molten form. Drum warmers may be required to obtain the molten state.

d. Economics

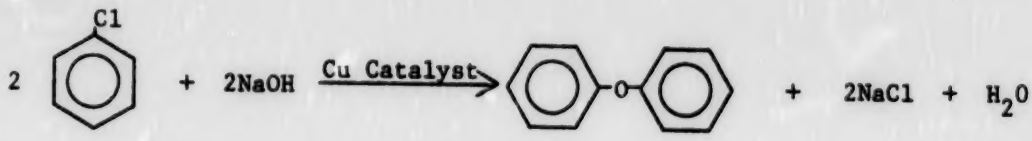
The following selling prices (1976) are for bulk shipments of diphenyl oxide:

industrial grade	$0.52/lb
technical grade	$0.60/lb
perfume grade	$0.85/lb

However, the large percentage of Dow's diphenyl oxide production is captively used to make Dowtherm® A, Dowfax® surfactants, butylchlorodiphenyl oxide, and decabromodiphenyl oxide. Since the diphenyl oxide is obtained as by-product, cost estimations are difficult.

In the expansion and revision of the chlorobenzene processes now underway at the Dow Midland facility, phenol production via chlorobenzene will be eliminated in favor of phenol production from cumene.

This would indicate that diphenyl oxide will be prepared directly from chlorobenzene and caustic soda. Dow held the original patent describing diphenyl oxide manufacture by this direct route (Hale, 1930). The chemistry of this reaction is:



The current selling prices of chlorobenzene and sodium hydroxide are $0.29/lb and $0.125/lb, respectively (Chemical Marketing Reporter, 1976). At a 90% yield, one pound of formed diphenyl oxide would consume $0.49 of raw materials. Since Dow makes the chlorobenzene and NaOH, cost would be considerably less than the selling price.

e. Environmental Management

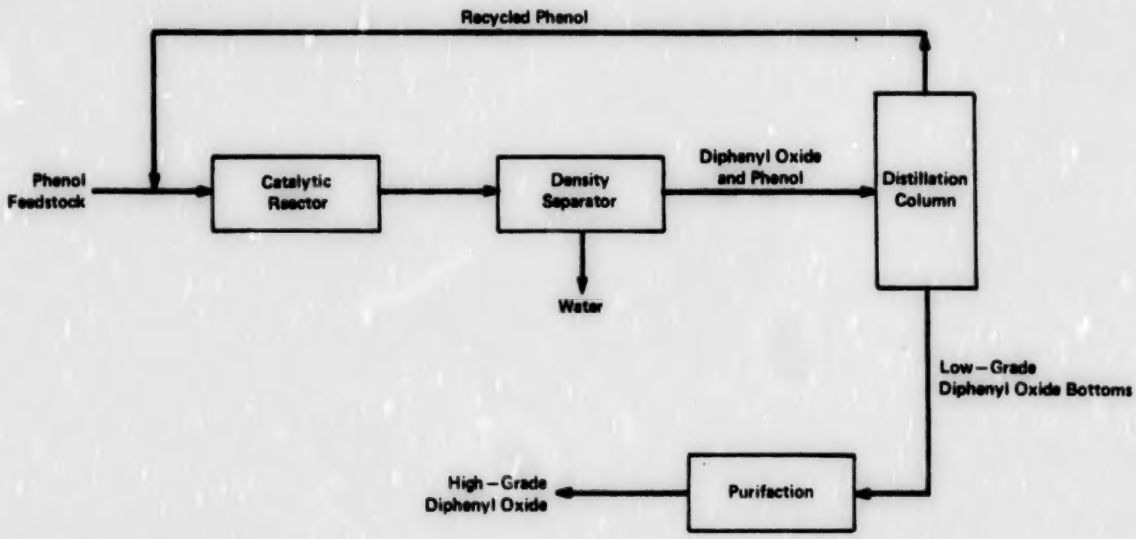
All diphenyl oxide-phenolic product losses in the sewer are treated by the Dow Chemical, Michigan Division, Waste Treatment Plant (Otis, 1976). Treatment efficiency for the diphenyl oxide in the Dow treatment plant is unknown.

2. Catalysis of Phenol

Monsanto Industrial Chemicals began producing diphenyl oxide at their Chocolate Bayou complex in Alvin, Texas in late 1975. Monsanto did not reveal any details concerning their process except that the overall process involves reacting phenol with catalysts.

The original description of producing diphenyl oxide by catalyzing phenol is contained in a German patent (Schöllkopf, 1929). The patent describes phenol as being heated to 350°C in an autoclave with activated fuller's earth to

give a 15% yield of diphenyl oxide. The process presently being used by Monsanto may be very similar. Undoubtedly, superior catalysts and techniques have been developed to increase reaction yields and rates which make the process economical. A simple flow-diagram illustrating this process would be:



The selective chemical reaction should be:

$$2\ C_6H_5OH \xrightarrow{\text{catalyst}} (C_6H_5)_2O + H_2O$$

The diphenyl oxide grade produced by Monsanto is 99.9% pure (Monsanto Technical Sheet IC/FF-49).

a. Production Volumes

Monsanto has been producing diphenyl oxide only since late

1975. Capacity or production volumes at the facility are not available as the information is considered proprietary. The large percentage of production will be used captively to make Therminol VP-1 (Pane, 1976), which is a heat transfer fluid of identical composition to Dowtherm® A. The unit which produces Therminol VP-1 was placed on-stream in early 1976 (Garza, 1976).

b. Environmental Management

Wastes generated by Monsanto's diphenyl oxide process are treated by the company's own waste treatment facility (Pane, 1976). The water by-product produced during the process will be included in the wastes treated by Monsanto. The efficiency of the treatment facility upon the diphenyl oxide wastes is unknown.

c. Economics

The current selling price (1976) of Monsanto's diphenyl oxide is $0.80/lb in bulk shipments.

Assume a 90% yield of diphenyl oxide from the phenol raw material and a phenol price of $0.27/lb (Chemical Marketing Reporter, 1976). Then 1 pound of formed diphenyl oxide consumes $0.332 worth of phenol.

V. Use and Use Process Technology

A. Biphenyl

1. Dye Carrier

At the present time, nearly 60% of the refined biphenyl produced in the U.S. is consumed in dyeing assistants called dye carriers. Polyester fibers, such as Dacron® and Terylene®, are difficult to dye because the polymers themselves are practically inert to most forms of chemical attack. To enable dyes to penetrate into these polyester fibers, the fibers must be treated with compounds which cause the fibers to swell. These swelling compounds, or "carriers" as they are usually called, are aromatic chemicals that improve the rate, color intensity, and uniformity of dyeing when added to the dyebath.

a. Manufacture

The companies who produce biphenyl are generally not the companies who formulate biphenyl into dye carrier products. Figure V-1 illustrates the overall schematic for the virgin polyester fiber-to-finished garment process. The companies who produce the dye carrier chemicals sell these chemicals to textile chemical specialty firms. Twenty-four of the larger textile chemical specialty firms who sell biphenyl products are identified in Table V-1.

The specialty firms receive the biphenyl chemical and add approximately 10% surfactants, or emulsifiers, which will render the water-insoluble biphenyl emulsifiable in the dyebath. Both nonionic and anionic emulsifiers are used with biphenyl to create the aqueous emulsions. The nonionic emulsifiers (condensation products of alkylphenols with ethylene oxide) are the most recommended types. However, a small amount of anionic emulsifier, such as sodium salts of naphthalene sulfonic acid, formaldehyde condensation

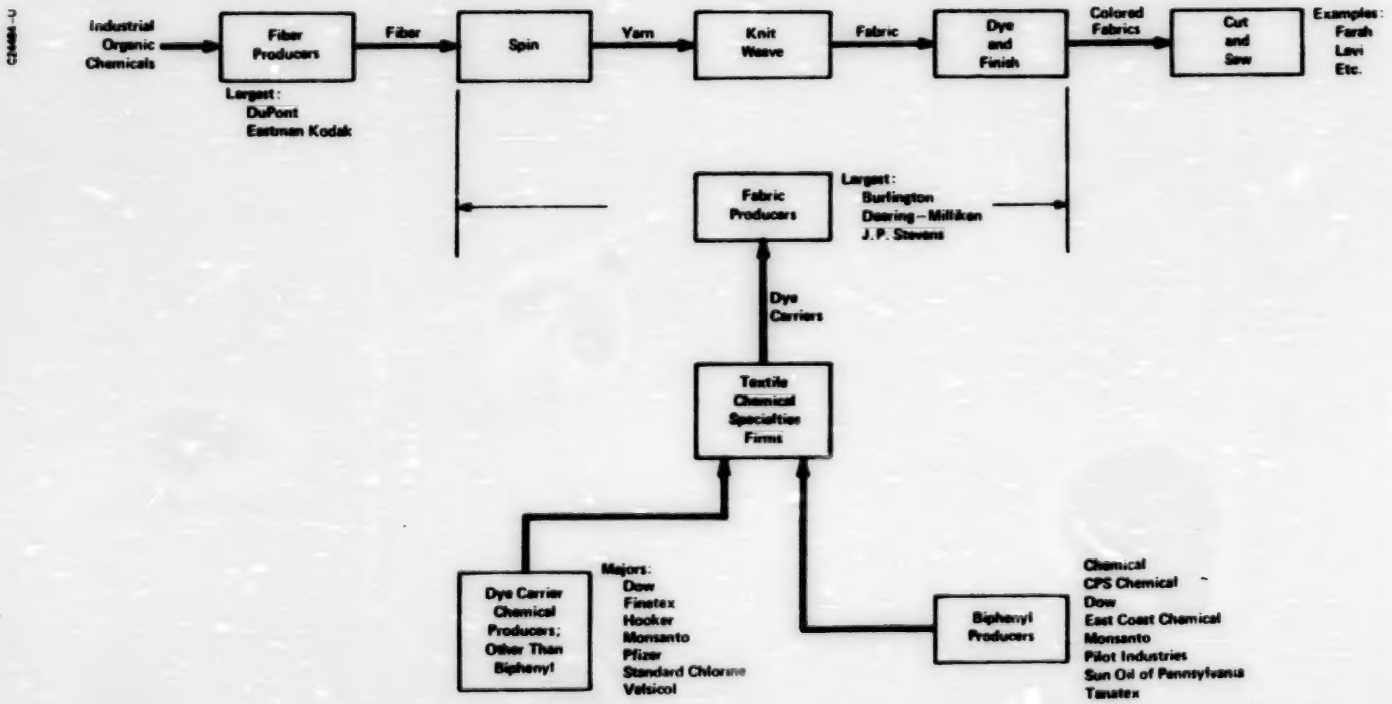


Figure V-1. Polyester Fiber to Garment Flow Diagram (adapted from Otis, 1976, and various personal communications)

Table V-1. Textile Chemical Specialty Firms Who Make Biphenyl Dye Carriers

	Firm	Site	Basic Product Name
1.	Arol Chemical Products Co.	Jersey City, NJ	Arosolve PC-7
2.	Chemical Processing of Georgia	Dalton, GA	Chemcryl COD Chemkar 209
3.	CNC Chemical Corp.	Central Falls, RI	Carrier A
4.	DePaul Chemical Co.	Long Island City, NY	Depco Jet Carrier 296
5.	W.F. Fancourt	Greensboro, NC	Neoport BT
6.	Finetex, Inc.	East Patterson, NJ	Accelerit BP
7.	High Point Chemical Corp.	High Point, NC	Carrier 100
8.	Independent Chemical Corp.	Brooklyn, NY	Speco Carrier 23
9.	Jordan Chemical Co.	Folcroft, PA	Jocar LOC
10.	Lutex Chemical Corp.	Chattanooga, TN	Super-Lok 845
11.	Millmaster Oxyx, Refined Onyx Div.	Lyndhurst, NJ	Decar BC
12.	Piedmont Chemical Ind.	High Point, NC	Carrier L-300
13.	Raytex Chemical Corp.	Charlotte, NC	Raycar LBP
14.	Richmond Oil, Soap & Chemical	Philadelphia, PA	Rocar 4921-A
15.	SAB Chemicals Co.	Jersey City, NJ	Sabcar #235
16.	Sandoz Color & Chemical	Hanover, NJ	Dilatin FBL
17.	A.E. Staley Mfg. Co.	Charlotte, NC	Charlab LBPW
18.	Standard Chemical Products	Charlotte, NC	Standye Car 180
19.	Star Chemical Inc.	Macon, GA	Carrier P-40
20.	Sun Chemical Corp.	New York, NY	Sunkem 660
21.	Tanatex Chemical Corp.	Lyndhurst, NJ	Carolid AL
22.	U.S. Oil Co.	East Providence, RI	Uscosist 810
23.	Virkler Chemical Co.	Charlotte, NC	Vircocarrier B
24.	Woonsocket Color & Chemical	Woonsocket, RI	Woonco Dye Assist M

products, sodium lignin sulfonate, and sulfonated turkey oil and other alkylaryl sulfonates, may be present to maintain proper dyeing levels. The surfactants added by each individual specialty firms are considered proprietary.

The biphenyl dye carrier product may also contain other common dye carriers, especially methylbiphenyl and chlorinated solvents. Methylbiphenyl is a common by-product obtained at the same time that biphenyl is refined from dealkylated toluene bottoms and has excellent dye carrier properties. The chlorinated solvents may include trichlorobenzene and perchloroethylene.

b. Dye Carrier Use

The textile chemical specialty firms, in turn, sell the biphenyl dye carrier products to the fabric producers and dyers, who are the ones who actually use the biphenyl product. As many as four to five hundred fabric dyers exist in the U.S. who use biphenyl as a dye carrier (estimate by industry spokesmen). Therefore, no effort was made to identify all dyers. However, industry spokesmen indicated that three particular fabric producers represented a "sizable" portion of the polyester market. Those three are:

(1) Burlington Industries
(2) J.P. Stevens, Inc.
(3) Deering-Milliken & Co.

The corporate offices of all three are located in New York City, and all have various plants situated throughout the United States. Burlington, for example, has mills located in Greensboro, Kernersville, and Rhodhiss, North Carolina and Roanoke, Virginia, in addition to 125 plants in the U.S.

Figure V-2 illustrates the general unit operations for dyeing and finishing polyester fabrics. The following stepwise procedure is recommended by Dow:

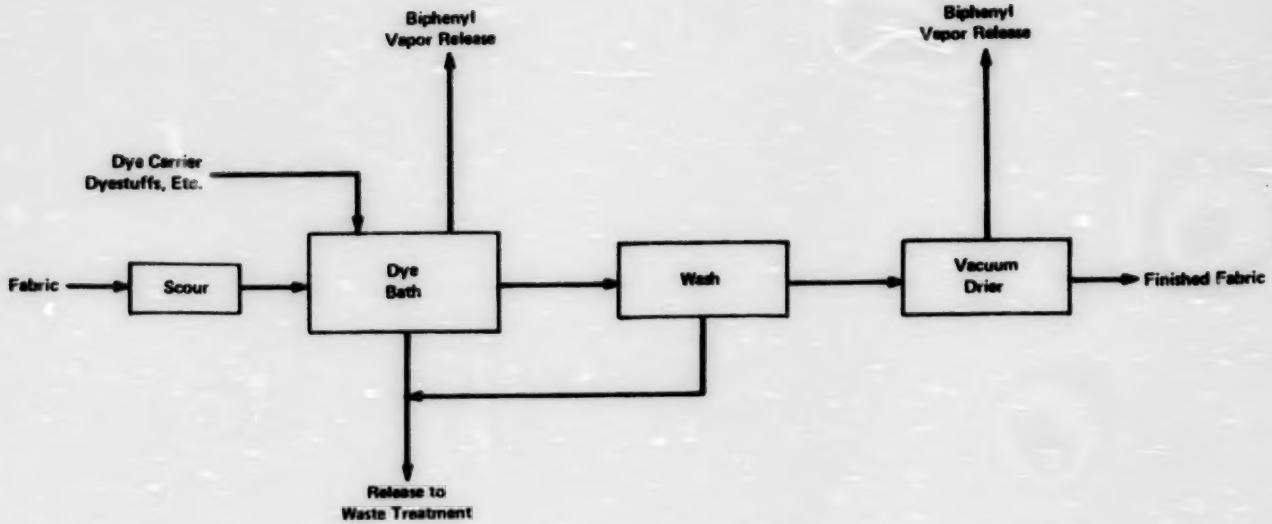


Figure V-2. Dyeing and Finishing of Polyester Fabrics

Step	#1	Water	25,000 lbs
	#2	Heat to 120°F	
	#3	Polyester Fabric	1,000 lbs
	#4	Sequesterant	15 lbs
	#5	Lubricant	10 lbs
	#6	Anionic Dispersant	10 lbs
	#7	Acetic Acid 70%	15 lbs
	#8	Dye Carrier	40 lbs
	#9	Disperse Dyestuffs	20 lbs
	#10	Heat to 260°F	
	#11	Run for 45 minutes	
	#12	Cool to 160°F	
	#13	Emulsified Perchloroethylene	25 lbs
	#14	Wash	

In general practice, the concentration of biphenyl varies from 3-12% of the weight of fabric (Carter, 1976; Monsanto Technical Bulletin 1C/FF-29). After washing, the fabric is dried and "heat set" in a vacuum drier. The dyebath liquor and wash water are released to waste treatment, which may be in-plant or city-county facilities.

c. Environmental Management

The dyebath vessel can either be pressurized or unpressurized. When dyeing at atmospheric pressure takes place, biphenyl vapors will be released from the dyebath. OSHA regulations permit a TWA (time weight average) of 0.2 ppm for biphenyl so dyers commonly use exhaust fans to vent biphenyl vapors to the outside atmosphere. After the fabric has been washed, it will still contain small amounts of biphenyl. The vacuum drier effectively removes this biphenyl, and the vapors are again vented to the outside. Small crystals of biphenyl may infrequently remain in the fabric after heat setting, but biphenyl's tendency to sublime under normal conditions leads to disappearance of these crystals.

At least 95% of the biphenyl added as dye carrier is released in the waste waters. Since the biphenyl is in an emulsified state, it

is too difficult to separate from the water; otherwise, it could be reused. It appears that most of the smaller dyers release their wastewaters directly to city-county sewage treatment facilities while several of the larger mills have on-site treatment (see Section IX-B-1).

d. Areas of Use

Nearly 22 million pounds per year of biphenyl dye carriers are estimated to be used in dyeing of polyester carpets and draperies in Georgia (Versar, 1976; Gaffney, 1976). This relatively small geographical area accommodates 250 to 300 mills representing 65% of the world's carpet and rug market.

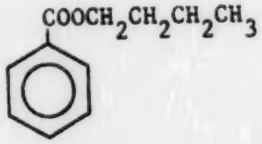
A similar quantity of biphenyl may well be used in the fabric mills of North Carolina. The textile mills of New England also use significant amounts of biphenyl.

e. Economics

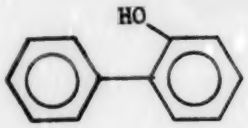
The biphenyl producers are currently selling 50-55 million pounds of biphenyl to the textile chemical specialty firms at a $0.16-$0.22/lb price. This would indicate annual sales of $8-12 million. The textile chemical firms process the biphenyl into dye carrier products and sell the products to the fabric dyers at a price which is often 100% and more, above the price which they paid for the biphenyl.

f. Alternative Products

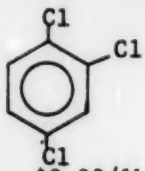
The following chemicals are all commercially used dye carriers which can be used in place of biphenyl:

(1) Butyl Benzoate - 

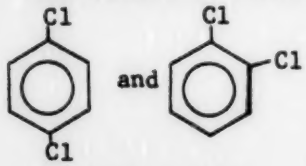
Selling Price: $0.30/lb (1976)
Manufacturers: CPS Chemical Co., Cindet Chemicals, Finetex, Velsicol, Pfizer, Tanatex

(2) o-Phenylphenol - 

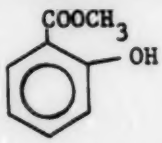
Selling Price: $1.50/lb (1976)
Manufacturer : Dow Chemical

(3) Trichlorobenzene - 

Selling Price: $0.39/lb (1976)
Manufacturers: Dow Chemical, Hooker, Standard Chlorine

(4) Dichlorobenzene - 

Selling Price: $0.31/lb (1976)
Manufacturers: Allied, Dow, ICC Industries, Monsanto, PPG, Solvent Chemical, Specialty Organics, Standard Chlorine

(5) Methyl Salicylate - 

Selling Price: $1.00/lb (1976)
Manufacturers: Dow, Monsanto, Tenneco

(6) Perchloroethylene - $Cl_2C = CCl_2$

Selling Price: $0.165/lb (1976)
Manufacturers: Diamond Shamrock, Dow, DuPont, Ethyl Corp., Occidental, PPG, Stauffer, Vulcan

(7) Methyl Naphthalenes -

Manufacturers: Crowley Hydrocarbon, Koppers, Marathon Oil

g. Alternative Processes

A commercial waterless dyeing process for textiles has been developed by Martin Processing Inc., Martinsville, VA. The company claims that, compared to conventional processes, it will eliminate water pollution, cut energy consumption in half, and reduce capital investment 60%. The process makes use of a combination of organic solvents maintained in a closed system within the equipment. Solvents are continuously purified and recycled, and no dyes are lost, the company says. According to Martin, which will market the process early in 1977 through its Temple Machinery Co. Division, the process is applicable to about half of the 14 billion yards of fabric piece dyed annually in the U.S. (Anon., 1976 c).

2. Biphenyl Fungicide in Fruit Packaging

Biphenyl has been used for nearly 30 years as a mild fungicide in citrus fruit wrappers and packaging. It would be impossible to ship citrus fruit across the U.S. or overseas in cartons, without a blue mold preventive like biphenyl. Years ago, "orange crates" of open lattice wood were used to let air circulate through and reduce mold formation. However, this exposed the fruit to the drying effects of air, external molds, water, dirt, etc. The new sealed cartons prevent all these problems, but absolutely require a mold retardant.

During the mid-1950's, the FDA investigated the toxicity of biphenyl. The Institute of Paper Chemistry (IPC) was chosen to determine analysis

methods and to investigate potential problems. As a result of the work by IPC, biphenyl was given a clean "bill-of-health" by the FDA (Versar, 1976).

a. Manufacture

The two American producers of biphenyl-impregnated papers are listed below:

(1) Crown Zellerbach Corp. San Francisco, CA

(2) Paper-Pak Corp. Orlando, FL

Biphenyl tissue wrappers are still manufactured as described in the original patent (Mispley and Barber, 1940). The biphenyl is bonded to the tissue paper by a solvent carrying the biphenyl; the solvent consisting of liquid paraffin oil fortified with paraffin wax. The tissue paper will contain about 1.75-2.97% of its weight as biphenyl and 7% to 9% of its weight as solvent.

Paper pads are impregnated in a similar fashion with 4 lbs of biphenyl per 1000 sq. ft. surface area (Cosner, 1976). Two pads are inserted into each container of fruit, one on top and one on bottom. The tissues are used to wrap each piece of fruit individually.

Efforts have been made to coat the insides of corrugated paper boxes with a biphenyl paste, but this method has yielded inferior protection. The air permeability of corrugated boxes allows the biphenyl to dissipate (sublime).

b. Production Volumes

Approximately 600,000 to 800,000 pounds of biphenyl are consumed for fungicide papers per year at present (Cosner, 1976). Production is seasonal, as would be expected from its use in fruit protection.

Ten years ago, at least several million pounds of biphenyl were annually consumed for fungicidal purposes. However, the advent of faster domestic transportation has lowered the need considerably. Today, a sizeable portion of the biphenyl papers produced are used for overseas shipments. Domestic use is still important, though, for long-haul shipment and closed container storage.

The amount of biphenyl used as a fungicide has been decreasing in recent years. Future projections indicate, at best, a stable market; however, slight decreases can be expected.

c. Economics

A high-grade purity biphenyl is required for fungicidal uses. The current selling price of Monsanto's high-grade biphenyl is $0.36/lb, indicating biphenyl sales for fungicides of $0.21 to $0.28 million annually. The sale of biphenyl papers may amount to several million dollars per year.

d. Environmental Management

The nature of this biphenyl use indicates that all of the biphenyl so used will eventually be exposed to the environment. A large percentage of biphenyl papers will eventually be disposed in solid trash disposals and/or incinerated.

e. Alternatives

One commercial alternative to biphenyl is o-phenylphenol (o-hydroxybiphenyl). Ortho-phenylphenol can be obtained as a by-product during Dow's phenol production from chlorobenzene, the same process from which diphenyl oxide was recovered. The o-phenylphenol is converted to the sodium salt which is used to control molds and rots of citrus and other fruits and for the

disinfection of domestic and agricultural buildings, warehouses, and refrigerated stores. Price is slightly higher than biphenyl, but its wider-range of protection is a definite advantage. It is an active ingredient in certain Lysol® cleaners.

3. Polychlorinated Biphenyl (PCB)

PCB production and use has been thoroughly studied in a previous EPA report (Versar, 1976), so only a brief review will be given here. This use of biphenyl has been stopped by Monsanto and no manufacturer is allowed to produce PCB's two years after the effective date (January 1, 1977) of the Toxic Substances Control Act (Section 6e, PL94-469).

a. Manufacture

Monsanto, the sole domestic manufacturer of PCB's, manufactured this chemical in their Sauget, Illinois plant. The PCB manufacturing operation is conducted in two steps. First, biphenyl is chlorinated with anhydrous chlorine in the presence of ferric chloride to produce crude PCB's and then the crude PCB's are distilled to obtain the finished product.

Until recently Monsanto made four different PCB products; Aroclor 1221, 1242, 1016, and 1254. The difference is in chlorine content which ranges from 21% in Aroclor 1221 to 54% in Aroclor 1254.

b. Production Volumes

Monsanto produced 40.4 million pounds of PCB's in 1974 and 8.5 million pounds in the first quarter of 1975 (Versar, 1976). The average chlorine content is roughly 48% when all PCB products are lumped together. Therefore, approximately 21 million pounds of biphenyl are consumed annually to produce PCB's.

c. Economics

Current selling price (1976) of PCB products averages about $6 per gallon (11.36 lbs/gallon). Total annual sales would therefore be nearly $11.1 million.

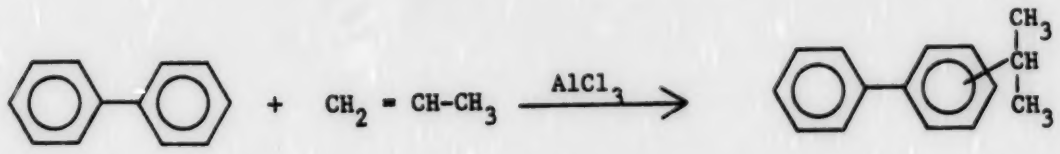
4. Alkylated Biphenyl

a. Isopropylbiphenyl

Commercially, isopropylbiphenyl is the most important of the alkylated biphenyls. Tanatex Chemical Division in Lyndhurst, NJ is the largest domestic producer of isopropylbiphenyl (Cohen, 1976); Pilot Industries of Houston, TX also manufactures the chemical (Barrow, 1976).

(i) Manufacture

Isopropylbiphenyl is manufactured by a Freidel-Crafts reaction of biphenyl with propylene, the chemistry being:



Primarily, the monoisopropyl derivative is formed, but small amounts of the diisopropyl derivative will also exist.

(ii) Production Volumes and Uses

Currently, about 10 million pounds of isopropylbiphenyl are annually produced (SRC estimation). Nearly all of the production is used in carbonless paper (Cohen, 1976). Manufacture started about 1971 and has accelerated to the present volume. In 1971, Monsanto terminated PCB's sales for carbonless paper, and isopropylbiphenyl has been used as a substitute for PCB in this application.

Isopropylbiphenyl may find future applications in heat transfer and capacitor fluids. It may be a component in Monsanto's proprietary dielectric fluid trade named "MCS-1238" (Versar, 1976). Monsanto has been testing "MCS-1238" as a possible PCB replacement.

(iii) Economics

The 1976 selling price of isopropylbiphenyl is $0.56/lb, which would indicate annual sales of $5.6 million to the carbonless paper industry.

b. Methylbiphenyl

Methylbiphenyl is obtained as a by-product when toluene is hydrodealkylated to benzene. It commonly exists as an impurity in the grade of biphenyl sold for dye carrier use; however, methylbiphenyl alone exhibits excellent dye carrier properties. Small quantities of methylbiphenyl are isolated and sold by Pilot Industries of Houston, TX, but commercial-scale production has yet to occur (Barrow, 1976).

Since methylbiphenyl has such good dye carrier properties, it is conceivable that efforts to synthesize it may have commercial importance in future years.

c. Ethyl- and Butylbiphenyl

Ethyl- and butylbiphenyl are produced by Freidel-Crafts reaction of biphenyl with ethylene and butylene, respectively. Pilot Industries produces small quantities for applications in heat transfer, but they are not commercially important yet (Barrow, 1976).

5. Eutectic Heat Transfer Fluid

See Section V-B-1.

6. Polybrominated Biphenyl (PBB)

PBB production and use has been studied in previous EPA reports (Mumma and Wallace, 1975; Neufeld et al., 1977), so only brief review will be given here.

a. Manufacture

Commercial production of PBB's was thought to have been terminated in 1974 (Mumma and Wallace, 1975), the commercial producers being Michigan Chemical Corp. of St. Louis, MI, and White Chemical Corp. of Bayonne, NJ. The suspected termination was precipitated when, in 1973, PBB's were inadvertently fed to dairy cows with harmful effects. However, decabromo- and octabromobiphenyl were commercially produced in 1975 and 1976 for export purposes by White Chemical (Bayonne, NJ) and by Fine Organics (Sayreville, NJ) (Neufeld et al., 1977).

The manufacturing process of PBB's is considered proprietary, but patent literature (Moore et al., 1974; Mitchell, 1973) describes production via bromination of biphenyl by bromine chloride or liquid bromine.

PBB's were used exclusively as flame retardants for plastics, and are currently exported for this purpose.

b. Production Volumes

Michigan Chemical produced a total of about 11.2 million pounds of PBB's during the period of 1970 to 1975, and White Chemical produced about 100,000 pounds of PBB's from 1970 to 1973. In 1976, 805 thousand pounds of PBB's were produced (Neufeld et al., 1977). The total production of PBB's from 1970 to 1976 was 13.334 million pounds.

c. Economics

The 1975 selling price of the major PBB product (Firemaster BP-6) was $0.75/lb. Combining this with the largest production year, 1974 (4.8 million pounds), reveals 1974 sales of nearly $3.6 million.

d. Alternatives

One viable alternative is decabromodiphenyl oxide (see Section V-B-6 for this discussion).

B. Diphenyl Oxide

1. Eutectic Heat Transfer Fluid

The major current use of diphenyl oxide is for manufacture of a eutectic heat transfer mixture composed of 73.5% diphenyl oxide and 26.5% biphenyl. This mixture has been marketed by Dow Chemical Co. as Dowtherm® A since the early 1930's. Dow produces Dowtherm® A in Midland, Michigan. Monsanto Industrial Chemicals, in Alvin, Texas, began producing an identical mixture called Therminol VP-1 ' early 1976. Dow and Monsanto are the only domestic producers; however, all of the known world producers of this particular mixture are listed below:

Producer	Country	Product
Dow Chemical	USA	Dowtherm® A
Monsanto	USA	Therminol VP-1
Imperial Chemical	Great Britain	Thermex
Nippon Steel Chemical	Japan	Therm S-300
Bayer	West Germany	Diphyl
Progil	France	Gilotherm

The biphenyl-diphenyl oxide eutectic mixture is used as both a heating and cooling heat transfer media. It is used in liquid phase at temperatures from 60°F to 750°F, and in the vapor phase at temperatures from 495°F to 750°F. It is non-corrosive, so carbon steel is usually selected for equipment in which it will be used. Physical properties of the mixture are listed on the Material Safety Data Sheets for Dowtherm® A in Appendix B.

The eutectic mixture is stable except at the upper temperature levels. The first decomposition effect of elevated temperatures is a polymerization to materials of higher molecular weight, but these polymers remain in solution in the liquid and do not affect operation as long as their concentration does not exceed 10%. At 750°F, the decomposition rate varies between 0.8% and 3.0% per 100 hours (Danziger, 1966). Dow has an analysis and purification service and can reprocess deteriorated Dowtherm if polymerization is not too advanced. Charles E. Sech - Consulting Associates (in Michigan) sells a purification

system to individual users of Dowtherm® A, which is nothing more than a single-plate distillation column. The impurities from the distillation are usually added to fuel oils because their heating value, as well as that of Dowtherm, is quite high (Sech, 1976).

a. Users

The eutectic mixture has numerous applications in synthetic fiber production and finishing, petroleum refining, and plastics manufacturing. About 2500 new installations, utilizing Dowtherm® A, were made in the U.S. from 1955-1965 alone (Danziger, 1966). It is virtually impossible to identify all users of the product as the use is so wide-spread.

b. Production Volumes

SRC estimates that approximately two-thirds of Dow's 1975 diphenyl oxide production (SRC estimation - 6 million pounds) was used to formulate Dowtherm® A. This would correspond to a 1975 production of slightly less than 5.5 million pounds of Dowtherm. Biphenyl use accounted for roughly 1.5 million pounds.

Dow is currently expanding their facilities which produce diphenyl oxide and Dowtherm® A. Estimates of future capacities are not available.

The capacity of Monsanto's new Therminol VP-1 unit is also not available. Due to the large available sources of the eutectic mixture overseas, the U.S. production is consumed domestically. It would seem unlikely that Monsanto's production in the near future would be larger than Dow's current production.

World-wide consumption of the eutectic mixture exceeded 1 million gallons (8.83 million lbs) in 1962 (Davies, 1963).

c. Economics

The following selling prices (1976) are for Dowtherm® A:

5 gallon pail	$0.84/lb
55 gallon drum	$0.79/lb
4000 gallon tankers	$0.66/lb

The 1975 sales of Dowtherm® A would roughly be $4 million considering a 5.5 million pound production.

d. Environmental Management

Occupational exposure to vapors of the eutectic mixture have been regulated by OSHA standards.

Manufacture involves only mixing of liquid diphenyl oxide and biphenyl. It seems unlikely that any quantity would be released to the environment during manufacture except by accidental spill or leak. Dow's "Material Safety Data Sheet" for Dowtherm® A calls for incineration of spilled materials (see Appendix B).

Users of the mixture can have contaminated quantities reprocessed by Dow or use old quantities as a burning fuel.

e. Use Alternatives

One of the major alternatives to Dowtherm® A is petroleum-derived oils. Numerous oils are included in this category and collectively, these petroleum-derived oils are probably the most widely used heat transfer media at temperature levels above that of moderate-pressure steam (up to 550°F). These oils are obtained as high-boiling fractions from petroleum. Several commercial products are listed below:

(1) Mobiltherm 600	Mobil Oil Co.
(2) Caloria 43	Exxon Corp.
(3) Security 205	Gulf Oil Corp.
(4) Tellus 7Z	Shell Oil Co.

Dowtherm® A has advantage over petroleum oils due to a higher film temperature which can be sustained before degradation occurs. Dowtherm® A is useable at temperatures up to 750°F, while the petroleum oils have a limit of 600°F. In addition, Dowtherm® A maintains a cleaner operating surface during normal use. The disadvantages of Dowtherm® A include a price differential in favor of the petroleum oils, and the extra cost of heat-tracing pipes as Dowtherm freezes at 54°F.

2. Dowfax®

Dowfax® is the tradename for dodecyldiphenyl oxide disulfonic acid, disodium salt manufactured by Dow Chemical in Midland, Michigan. Dowfax® surfactants are anionic wetting agents of the sulfonate type which are used in latex production, agricultural formulations, cleaning compounds, dye assists, detergents, and in textile fiber production (Dow Products & Services Catalog).

a. Manufacture

A flow diagram illustrating the manufacture of Dowfax® is shown in Figure V-3.

Diphenyl oxide is alkylated with either n-dodecyl chloride or 1-dodecene to dodecyldiphenyl oxide. The dodecyldiphenyl oxide is dissolved in an organic solvent, and sulfonation is carried out with SO_3. The chemical reaction is:

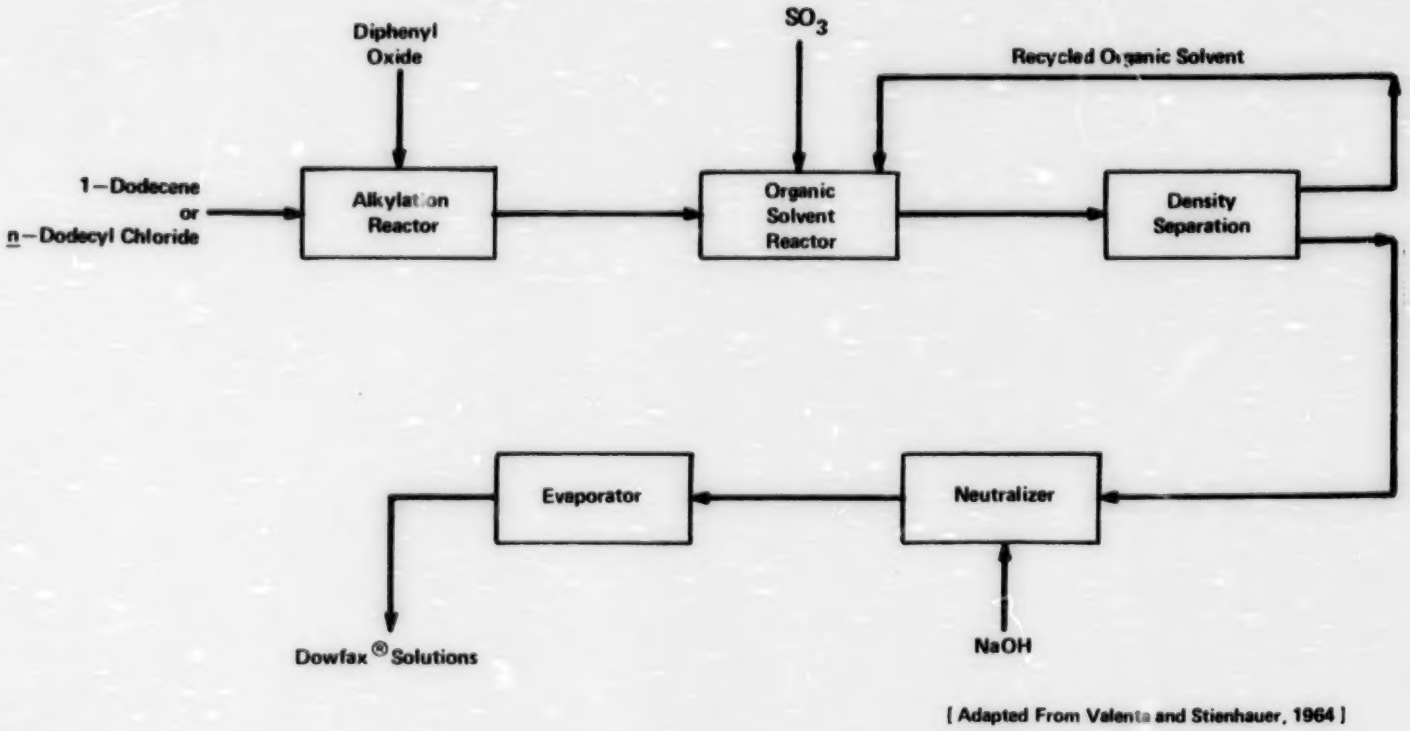


Figure V-3. Process Manufacture of Dowfax® Solutions

The solution is allowed to density separate and the upper layer of organic solvent is decanted. An aqueous NaOH solution is now added to the bottom layer to neutralize the dodecyldiphenyl oxide disulfonic acid to the disodium salt. Evaporation of the solution to dryness gives a buff to white powder of dodecyldiphenyl oxide disulfonic acid, disodium salt (Valenta and Steinhauer, 1964; Branson, 1977).

Several Dowfax® products are available from Dow:

(1) Dowfax® 2A1 Surfactant Solution
(2) Dowfax® 3B2 Solution
(3) Dowfax® 2AO

(1) and (2) above are sodium salt solutions containing 45% active ingredient of mono and di alkyldiphenyl oxide disulfonate, where the alkyl group is C_{12} and C_{10}, respectively. (3) Is the acid form (not neutralized with NaOH).

b. Production Volumes

Production volumes were not available from Dow; however, SRC estimates that Dow captively consumes about 0.75 million pounds annually of diphenyl oxide to synthesis Dowfax® surfactants. This would mean an annual production of roughly 2.3 million pounds of Dowfax® surfactants. Dow introduced this product in the early 1960's. Projections for future growth were not obtained.

c. Economics

The selling price (1976) of Dowfax® 2A1 Surfactant Solution is $0.47/lb; therefore, the selling price of the dry powder dodecyldiphenyl oxide disulfonic acid, disodium salt would be approximately $1.00/lb. This would indicate annual sales of $2.3 million.

d. Environmental Management

It is doubtful if significant quantities of diphenyl oxide are released to the environment via manufacture of Dowfax®. Sewer wastes

containing diphenyl oxide are treated by Dow's Michigan Division Waste Treatment Plant (Otis, 1976). Treatment efficiency of the plant with respect to diphenyl oxide is unknown.

e. Alternative Products

There are numerous surfactants commercially available on the American market. Many are organic derivatives of high molecular weight alkyl sulfates or sulfonates. Dowfax® can be included in the group of surface-active agents having ester or ether linkages. Other chemicals included in this group are:

(1) Sulfosuccinic acid esters
(2) Coconut oil acids, 2-sulfoethyl ester, sodium salt
(3) Dodecyl sulfoacetate, sodium salt
(4) Herring oil, sulfonated, sodium salt
(5) Isooctylphenol, ethoxylated and sulfonated, sodium salt
(6) n-Octylphenol, ethoxylated and sulfonated, sodium salt

Selling prices on the above vary from $0.55 - $1.00/lb.

3. Diphenyl Oxide Dye Carriers

Diphenyl oxide dye carriers were made commercially available in the U.S. in 1973. Dow Chemical supplies the "industrial" grade diphenyl oxide to the textile specialty chemical firms as described for biphenyl dye carriers (see Section V-A-1). This industrial grade assays 90% diphenyl oxide and the remainder as methylnaphthalenes and naphthalenes (Dow Form No. 110-288-72). Diphenyl oxide is used the same as biphenyl as a dye carrier.

The textile chemical specialty firm which apparently handles most of the diphenyl oxide dye carriers is Chemical Processing of Georgia in Dalton, Georgia.

a. Volume of Use

Company spokesmen for Chemical Processing of Georgia estimate

diphenyl oxide dye carrier use at much less than one million per year currently. No great increase is expected in the near future.

SRC estimates the current use of diphenyl oxide in dye carriers at roughly 0.25 million pounds per year.

b. Economics

Recent selling price (1976) for Dow "industrial grade diphenyl oxide is $0.52/lb, up from $0.32/lb in 1973. After the chemical specialty firms add emulsifiers and proprietary ingredients, the cost to the textile dyers may be 100-200% greater. This would make the total sales of diphenyl oxide dye carriers in the neighborhood of $0.35 million per year.

c. Environmental Management

Same as for biphenyl. See Section V-A-1.

d. Alternative Products

Same as for biphenyl. See Section V-A-1.

4. Perfumes and Soaps

Due to its characteristic geranium odor, diphenyl oxide has been used in perfume formulations since the early 1930's.

a. Manufacture

The major manufacturers of diphenyl oxide perfumes are:

(1)	Givaudan Corp.	Clifton, NJ
(2)	Florasynth, Inc.	New York, NY

Actual compositions of perfume products are considered proprietary; however, the concentration of diphenyl oxide in the final products is listed below (Opdyke, 1974):

Concentrations in %

	Soap	Detergent	Creams, Lotions	Perfume
Usual	0.05	0.005	0.05	0.15
Maximum	0.20	0.03	0.10	0.40

The largest user of diphenyl oxide in soaps and detergents has been suggested to be Proctor & Gamble Company, corporate offices in Cincinnati, Ohio.

Before compounding the "perfume" grade diphenyl oxide into perfumes, it is common to increase the purity by chemical means (Mahinka, 1976). Crystallization is probably the most common method.

b. Volume of Use

Recent estimates of diphenyl oxide use in fragrances in the U.S. amounts to about 100,000 lbs/yr (Opdyke, 1974). This figure is down from 200,000 lbs/yr in 1965 (Cantrill, 1968). The 100,000 lbs/yr figure is expected to remain stable in the near future.

Nearly one-half of the diphenyl oxide currently used in fragrance products is imported. In 1974, 43,201 pounds of diphenyl oxide were imported for this use (United States International Trade Commission, "Imports of Benzenoid Chemicals and Products 1974"). Before 1974, there is no record of any imports.

c. Economics

The selling price (1976) for "perfume" grade diphenyl oxide is $0.85/lb, which is up from $0.51/lb in 1965. After formulation into fragrance products, the price will be many times greater.

d. Environmental Management

The nature of fragrance products indicates that all 100,000 lbs/yr use will be exposed to man and the environment. It should be noted that biological data (Opdyke, 1974) suggest no adverse effects due to human use of diphenyl oxide in perfumes and soaps.

e. Alternative Products

Perfume formulators (Mahinka, 1976; Graham, 1976) cite many aromatic ethers which are useable in perfumes. The only reason diphenyl oxide is chosen in certain instances is its relatively low cost compared to alternatives.

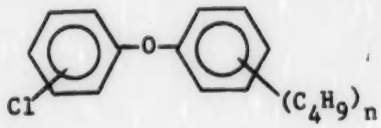
5. Butylated Monochlorodiphenyl Oxide

Butylated monochlorodiphenyl oxide has recently been marketed by Dow Chemical in Midland, Michigan, under the tradename "XFS-4169L". Dow hopes that this product will be a viable alternative to PCB's used in capacitors. In September 1975, Dow began manufacturing XFS-4169L in pilot-quantities for use by McGraw-Edison and other U.S. capacitor producers (Anon., 1976 b) and is in the process of expanding capacity.

a. Manufacture

Specific details of manufacture were not available from Dow, but production is probably accomplished by monochlorination of diphenyl oxide followed by butylation. Monochlorination of diphenyl oxide is described in a Dow patent (Hennis, 1974). According to the patent, diphenyl oxide, containing 0.005 moles of 98% H_2SO_4 as catalyst, is chlorinated to yield the following products: 8% o-chlorodiphenyl oxide, 67% p-chlorodiphenyl oxide, 10% dichlorodiphenyl oxide, and 15% unreacted diphenyl oxide.

The monochlorodiphenyl oxide can be butylated by Freidel-Crafts reaction ($AlCl_3$ catalyst) with butene or butyl chloride. The general formula for XFS-4169L is (Branson, 1975):



$n = 0,1,2,3$

b. Production Volumes

Until 1976, only pilot-quantities of XFS-4169L were being produced, but Dow assured the electrical industry that it would have a capacity rate of one million pounds per year during the first quarter of 1976 (Branson, 1975). Dow now says (Anon., 1976 b) that it hopes to have production capacity in excess of 5 million lbs/yr by the end of 1976. Five million pounds of butylated monochlorodiphenyl oxide would consume roughly 3 million pounds of diphenyl oxide. The diphenyl oxide and chlorobenzene expansion presently under construction at Dow is designed to produce the additional capacity of required diphenyl oxide.

c. Environmental Management

Sewer wastes containing diphenyl oxide are treated by Dow Michigan Division Waste Treatment Plant (Otis, 1976); however, significant quantities of diphenyl oxide should not be released from the XFS-4169L process as unreacted diphenyl oxide can be recycled for chlorination. Specific environmental management techniques concerning the chlorodiphenyl oxides were not obtained from Dow.

d. Economics

1976 selling prices of XFS-4169L range from $21.50 to $30 per gallon depending upon volume; least expensive for 55 gallon drums, most

expensive for 5 gallon pails. Large scale production figures to lower the selling price to $12 per gallon ($1.40/lb). If 5 million pounds per year are sold, this would represent sales of $7 million.

e. Alternatives

Butylated monochlorodiphenyl oxide was developed to be an alternative to the toxic and persistent PCB's, which sell for $6-$7 per gallon. However, because of environmental contamination resulting from their use, PCB's will no longer be produced in the future. Many corporations are presently involved in research and testing of new compounds to replace PCB's. Some of the primary possibilities have been summarized in a previous EPA - Office of Toxic Substances Report (Versar, 1976); they are listed below:

(1) Dioctyl Phthalate
(2) Diisononyl Phthalate
(3) Isopropyl Dichlorobiphenyl
(4) Silicones
(5) Diaryl Sulfone

6. Decabromodiphenyl Oxide

Decabromodiphenyl oxide (decabromodiphenyl ether, decabromophenoxylbenzene) is used as a flame retardant in certain types of flame resistant polystyrene, polypropylene, polybutylene, terephthalate, ABS resins, and other plastic materials (Levek and Williams, 1975).

a. Manufacture

The four domestic producers of decabromodiphenyl oxide are:

Producer	Site	Tradename
(1) Dow Chemical Co.	Midland, MI	FR-300-BA
(2) Great Lakes Chemical Corp.	El Dorado, AR	Great Lakes DE-83
(3) Hexcel Corp., Fine Organics, subsid.	Sayreville, NJ	--
(4) White Chemical Corp.	Bayonne, NJ	--

Details concerning actual manufacturing methods are considered proprietary and are not available. A survey of patent literature revealed no information concerning decabromodiphenyl oxide production. A Dow patent (Moore et al., 1974) describes bromination of biphenyl with bromine chloride. Decabromobiphenyl is obtained by adding a stoichiometric excess of bromine chloride, under pressure in a closed vessel, to biphenyl in the presence of an $AlCl_3$ catalyst. Decabromodiphenyl oxide could conceiveably be prepared by a similar method. The bromine content in decabromodiphenyl oxide is nearly 83% by weight (Tabor, 1973).

b. Production Volumes

SRC estimates that roughly 0.5 million pounds of diphenyl oxide are presently consumed per year to produce decabromodiphenyl oxide. This would correspond to an annual decabromodiphenyl oxide production of 2.8 million pounds. Commercial production of decabromodiphenyl oxide began in 1972.

Company spokesmen are projecting increases in production during the next several years; an exact percentage was not available.

c. Economics

Decabromodiphenyl oxide (Dow's FR-300-BA) is currently selling (1976) for $1.80/lb, which is up from $1.08/lb in 1973. Annual sales could amount to nearly $5 million.

d. Environmental Management

Wastes from decabromodiphenyl oxide production units should contain only small amounts of diphenyl oxide. The total diphenyl oxide which may be exposed by these units is probably insignificant when compared to other diphenyl oxide uses. Effectiveness of diphenyl oxide waste treatment is discussed in Section IX-B-2.

e. Alternatives

Several years ago, polybrominated biphenyls (PBB's) were an important commercial flame retardant. Decabromodiphenyl oxide was developed to compete with PBB's for various applications, but decabromodiphenyl oxide cost nearly twice as much as PBB's. However, domestic PBB production was terminated in November 1974, after dairy cattle were mistakenly fed a PBB product (Mumma and Wallace, 1975). PBB's are still produced for export (Neufeld et al., 1977).

One of the new flame retardants, with applications similar to decabromodiphenyl oxide, is Citrex BC-26, sold by Cities Service Company in Rockville, Conn. (Mumma and Wallace, 1975). Citrex BC-26 is a halogenated organic containing 29% bromine and 40% chlorine with a price comparable to decabromodiphenyl oxide.

Other comparable flame retardants include (Tabor, 1973):

(1)	Tetrabromobisphenol-A	$0.57/lb
(2)	Pentabromochlorocyclohexane	$1.10/lb
(3)	Dibromoneopentyl Glycol	$0.55/lb
(4)	Tris (2,3-dibromopropyl)phosphate	$0.65/lb

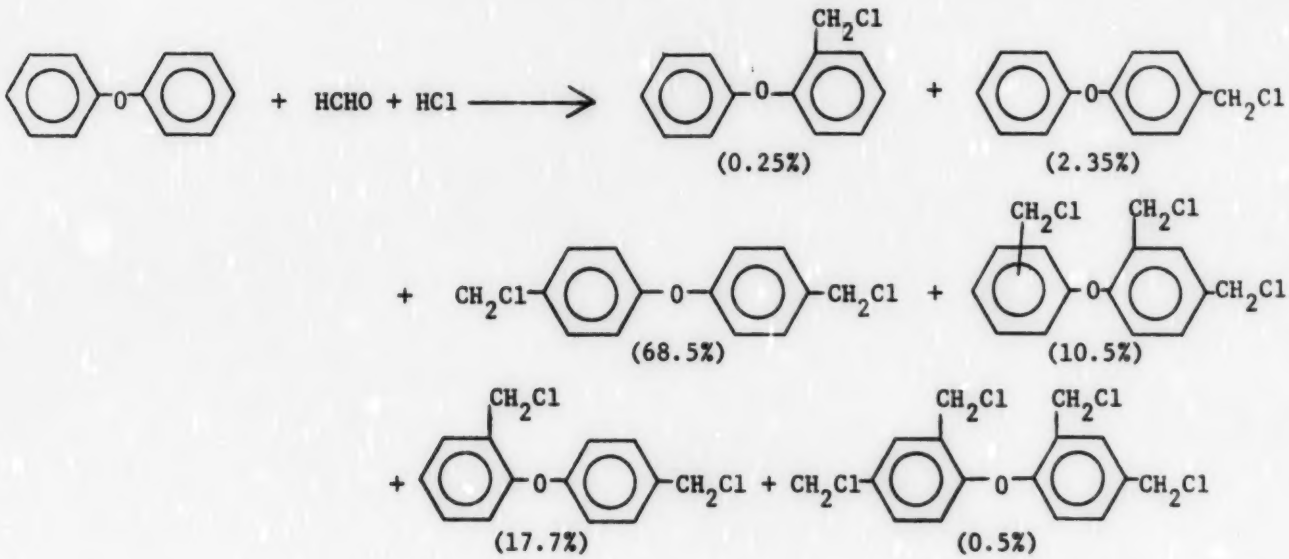
7. Minor Commercial Uses of Diphenyl Oxide

a. Chloromethyldiphenyl Oxide

Chloromethyldiphenyl oxide and di(chloromethyl)diphenyl oxide are produced in small quantities and are used to make thermosetting foams and resins.

The production technology was developed by Dow Chemical (Doedens and Rosenbrock, 1961), but the only U.S. producer of chloromethyldiphenyl oxide and di(chloromethyl)diphenyl oxide is Stauffer Chemical in Edison, NJ (Insera, 1976). Stauffer has produced these chemicals since 1971.

Diphenyl oxide reacts with formaldehyde and hydrochloric acid to produce a variety of chloromethylated compounds. The degree of chlorination determines the distribution of isomers. Chloromethylation to 25.2% chlorine, for example, would produce the following isomer distribution (Dow Form No. 110-288-72):



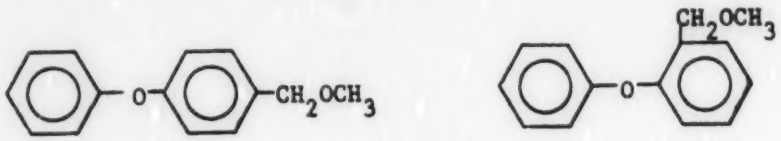
Pure materials can be recovered by use of solvent extraction and distillation (Doedens and Cordts, 1961).

The total combined production of chloromethyl and di(chloromethyl)diphenyl oxide amounts to much less than 100,000 pounds per year (Insera, 1976). Initial hopes for large-scale production have failed to materialize and significant growth in the future is not forecast.

b. Methoxymethyldiphenyl Oxide

Methoxymethyldiphenyl oxide is also produced by Stauffer Chemical in Edison, NJ. Production volumes are less than those for chloromethyldiphenyl oxide (Insera, 1976).

Diphenyl oxide and formaldehyde are used as the starting materials to produce methoxymethyldiphenyl oxide. Various isomers are formed, as shown for chloromethyldiphenyl oxide. The mono-para and mono-ortho isomers shown below make-up the bulk of production.

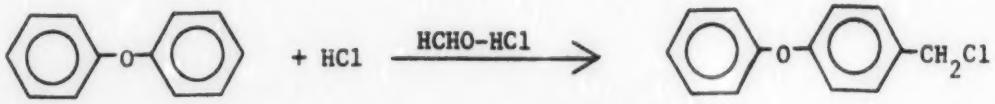


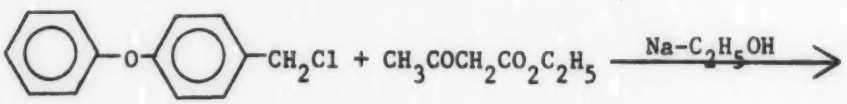
Methoxymethyldiphenyl oxide is used to manufacture Westinghouse's Doryl resins (Cogley, 1976). Doryl resins are used in high temperature varnish applications for electrical insulators.

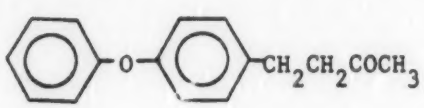
c. Pesticides

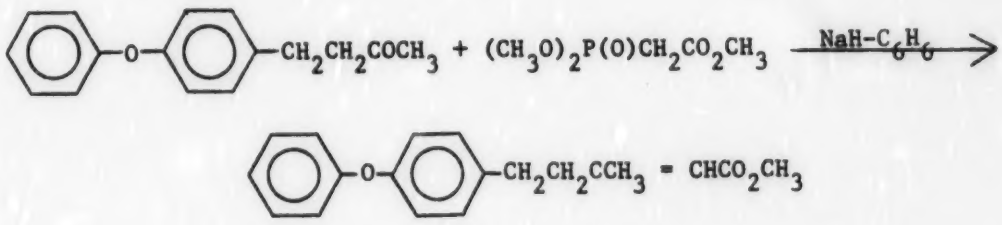
Diphenyl oxide has been identified in a pesticide plant's raw effluent (Webb et al., 1973) via gas chromatography - mass spectrometry. A survey of patent literature revealed that Ciba-Geigy Corporation holds patents describing insecticide production from diphenyl oxide. However, the Ciba-Geigy pesticide production facilities (in McIntosh, Alabama) failed to respond to inquiries asking about diphenyl oxide use, perhaps due to proprietary considerations.

The following synthesis is an example of diphenyl oxide use in insecticides detailed in a Ciba-Geigy patent (Franke and Traber, 1972):

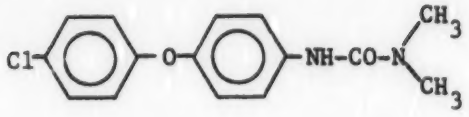
(1) 

(2) 

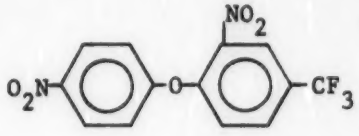


(3) 

Ciba-Geigy has marketed the following pesticides with a diphenyl oxide moiety:



(Chloroxuron)



(Fluorodifen)

It is doubtful that the above pesticides are synthesized with diphenyl oxide as a raw material, but diphenyl oxide may be generated in by-product amounts large enough to detect via gas chromatograph - mass spectrometer. This may account for the identification of diphenyl oxide in pesticide effluents, but this is only speculation. We have not been able to determine if diphenyl oxide is definitely used as a raw material for pesticide production, and this possibility still exists.

VI. Sources of Biphenyl and Diphenyl Oxide Occurring in Nature

A. Biphenyl

1. Petroleum

Aromatic compounds of almost every known type have been found in petroleum. Biphenyl and its three mono-methyl derivatives have been identified and isolated from crude petroleum (Hunt and O'Neal, 1967).

Biphenyl, which boils at 255°C, was isolated in the dinuclear aromatic portion of petroleum boiling in the range 255° to 275°C. Mair and Mayer (1964) have estimated that biphenyl makes up 0.008% by volume of crude petroleum. In 1973, 3.1×10^9 barrels of crude oil were produced in the United States (SRI, 1975 b). This translates to approximately 1.3×10^{11} gallons of crude oil of which an estimated 0.008% by volume was biphenyl. Converting to weight measurement, an estimated 80 million pounds of biphenyl were present as a naturally occurring constituent of the petroleum domestically produced in 1973. In addition, nearly 5×10^{10} gallons of crude petroleum were imported in 1973 (SRI, 1975 b), which may have contained an estimated 30 million pounds of biphenyl. Note that the combined total of biphenyl content in domestically produced and imported crude oil, 110 million pounds, is slightly higher than the amount of biphenyl which is refined annually, 85 million pounds (SRC estimation). The biphenyl which is present in petroleum appears to be used in fuels because it is not refined; 0.008% is much too small to recover.

It has been estimated that the total oil influx into the ocean from routine discharges from tankers, accidents in port and on the high seas in exploration and production, in storage, in pipeline breaks, from spent lubricants, from incompletely burned fuels, and from untreated industrial and domestic

sewage is between 11 - 12,000 million pounds per year (Blumer et al., 1971). Assuming 0.008% by volume biphenyl content, simple calculation suggests that approximately 1,000 pounds of biphenyl are annually released into the environment with spilled oil.

Methylbiphenyls amount to an estimated volume %, relative to crude petroleum, of approximately 0.0404% (Mair and Mayer, 1964; Yew and Mair, 1966). This amounts to five times the volume of plain biphenyl.

2. Foods

Stevens et al. (1966) identified biphenyl in the volatile constituents of grapes by use of a capillary gas chromatograph attached to a mass spectrometer. Biphenyl had previously been identified in orange volatiles by Schultz et al. (1964); however, Schultz et al. attributed the biphenyl's presence to packaging materials which were impregnated with fungistat biphenyl. The grapes used by Stevens in his investigation were handled in bulk, and fungistat biphenyl could not have come from packaging. It would seem possible, therefore, that biphenyl may be a naturally occurring constituent of grape volatiles.

Kinlin et al. (1972) identified biphenyl in the volatile constituents of roasted filbert nuts while Walradt et al. (1971) found biphenyl in peanut volatiles. Stoll et al. (1967) identified biphenyl as one of 202 constituents present in coffee concentrate.

The amounts of biphenyl which may occur in foods are very small and it is very doubtful if any significant quantities of biphenyl are exposed to the environment via this route.

B. Diphenyl Oxide

1. Plants

In addition to biphenyl, Stevens et al. (1966) identified diphenyl

oxide in the volatile constituents of grapes. Kimland et al. (1972) identified diphenyl oxide as one of many compounds present in Greek tobacco.

The amounts of diphenyl oxide which may be released to the environment from plants are probably very small.

VII. Generation of Biphenyl and Diphenyl Oxide By-Products

Section IV (General Manufacturing and Production Technology) discussed the processes by which biphenyl and diphenyl oxide by-products are obtained and refined commercially. This section examines biphenyl and diphenyl oxide generation in processes in which they are not refined or intended to be refined.

A. Biphenyl

1. Dealkylation of Toluene

The commercial producers of refined biphenyl, from the dealkylated toluene by-product, are identified in Section III (Production) and Section IV-A-1, along with the petrochemical company sources of the by-product. The companies listed below also produce benzene by dealkylating toluene; however, they do not refine the biphenyl stream or sell it to refiners.

Company	Site
1. Ashland Oil Co.	Cutlettsburg, KY
2. Crown Central Petroleum Corp.	Houston, TX
3. Enjay Chemical Co. (Exxon)	Baytown, TX
4. Leonard, Inc.	Mount Pleasant, MI
5. Monsanto	Alvin, TX
6. Shell Oil Co.	Odessa, TX
7. Signal Oil & Gas Co.	Houston, TX
8. South Hampton Co.	Stilsbee, TX
9. Sunray-DX	Tulsa, OK

The biphenyl streams generated by the above companies are added to fuels, usually fuel oils. The amount of biphenyl added to fuels via toluene dealkylation totals nearly 20-25 million pounds annually (SRC estimation).

2. Naphthalene Feedstocks

Most of the naphthalene produced by petroleum operators is petroleum-derived. Naphthalene and/or naphthalene precursors occur in

*Hahn, 1970, p. 411-412

significant quantities in the following petroleum-derived streams (Erskine, 1970), and the streams are used as naphthalene feedstock to produce a purified naphthalene.

(1) Petroleum streams are catalytically reformed with the intention of producing high-octane motor and aviation gasoline, and it is possible to operate the reformer to yield heavy "bottoms" that contain a high portion of methylnaphthalenes and naphthalenes. Biphenyl is found as a by-product in the "bottoms".

(2) Catalytic cracking is used to convert heavy petroleum fractions into lighter gasoline components, and one of the products of cracking contains naphthalene precursors. Biphenyl is also formed during cracking.

The typical composition of naphthalene feedstocks obtained from catalytic reformates and cracking are (Doelp, 1966):

	Catalytic Reformates (Wt %)	Catalytic Cracking (Wt %)
biphenyl & acenaphthenes	6%	6%
alkylnaphthalenes	55%	35%
alkylbenzenes	20%	25%
other aromatics	19%	34%

Naphthalene is obtained by hydrodealkylating the alkylnaphthalenes by the same method as previously described for hydrodealkylating toluene to benzene (Section IV-A-2). Once again, the biphenyl by-product which is produced will probably be added to fuels.

3. Coal Tar

Biphenyl was first identified in the high-boiling fractions from coal tar distillation in 1875 by Büchner (Poffenberger, 1950). Coal tar amounts to about 3% by weight of the coal which is processed. Along with many other hydrocarbons, biphenyl is part of the high-boiling fractions, distilling in the range 250°-300°C; however, no chemicals are separated commercially from this range. A fraction distilling mainly in the range 240°-270°C is employed at coking installations as wash oil for scrubbing benzole from coal gas, but most of the oils in this range are used in creosote blends (McNeil, 1969). These creosote oils are used for coating wood as a preservative, usually on railroad ties and telephone poles. Due to the nature of this use, any biphenyl content of the creosote oil will be exposed to the environment from weathering effects, which may leach or vaporize the biphenyl from the treated wood.

Approximately 160 million gallons of creosote oil are consumed annually (SRI, 1974). Dolansky (1974), in an analysis of creosote oil, determined that 60% of the oil was composed of a hydrocarbon fraction and that 1.35% of the hydrocarbon fraction was biphenyl. Applying Dolansky's figures to the U.S. consumption of 160 million gallons of creosote oil annually reveals that approximately 10 million pounds of biphenyl are contained in this consumption. It is probably reasonable to assume that the bulk of this biphenyl will be exposed to the environment.

In 1974, 677 million gallons of coal tar were produced domestically (United States International Trade Commission). Excluding that portion of the coal tar distilled to creosote oils, the coal tar probably contained from several to 10 million pounds of biphenyl which apparently ended up in fuels or coking operations, but this is not known for certainty.

4. Automobile Exhaust

It is likely that biphenyl is a component of the exhaust gas emitted by an automobile engine; however, there is no proof in the literature to support this supposition. Schofield (1974) lists the various hydrocarbon components identified in auto emissions, which he obtained from the General Motors Research Laboratories. The hydrocarbon list contains 1.11% by volume of unidentified aromatics, and it may be possible that biphenyl is included in these unidentified aromatics. Schofield does identify the presence of benzene at a volume concentration of 2.15%, and at the elevated temperatures of an automobile engine it is possible that the benzene could react chemically to form biphenyl. Section IV-A-1 describes Monsanto's commercial production of biphenyl by passing benzene vapors through a thermal reactor.

The total emissions of hydrocarbons from transportation sources was estimated to be 29,400 million pounds in 1971 (Council on Environmental Quality, 1973). If even a fraction of a percent of these emissions is biphenyl, sizeable quantities could be released directly to the environment.

B. Diphenyl Oxide

1. Caprolactam - Nylon Production

Over 90% of the caprolactam produced in the U.S. is used to manufacture Nylon 6. The following data suggest that diphenyl oxide is formed as a by-product during the production of caprolactum or its precursors: (1) Phenyl ether (diphenyl oxide) has been identified in a settling pond of a nylon plant in concentrations of 0.05 mg/l (Webb et al., 1973); and (2) diphenyl oxide has been isolated as an impurity in technical caprolactam in concentrations of 10 ppm (Kolar and Klacel, 1962).

Caprolactam is commercially synthesized from processes based on cyclohexanone. It is difficult to predict any diphenyl oxide by-product formation during these processes. However, cyclohexanone is prepared, in one commercial process, by catalytic hydrogenation of phenol. Phenol can be catalyzed to produce diphenyl oxide, as shown by Monsanto's commercial method. It may, therefore, be possible that diphenyl oxide is formed in small amounts during the manufacture of cyclohexanone via phenol.

2. Bituminous Coal Tar

Diphenyl oxide has been identified as one of 133 individual compounds present in bituminous coal tar (Karr et al., 1967). The fate of diphenyl oxide which may be present in coal tar is unknown.

VIII. Material Balance - Exposure to the Environment

This section attempts to define quantitatively the amounts of biphenyl and diphenyl oxide released to the environment by man. Only uses which are releasing or could potentially release substantial amounts of biphenyl and diphenyl oxide to the environment are discussed. The following areas are not discussed because quantities which may be released are insignificant by comparison: production of refined biphenyl and diphenyl oxide and chemical synthesis (PCB's, alkylated biphenyls, Dowfax^{R}, butylated monochlorodiphenyl oxide, decabromodiphenyl oxide, chloromethyldiphenyl oxide, or pesticides).

A. Biphenyl

Table VIII-1 lists the estimated environmental releases of biphenyl. Explanations of the high-low estimates are given below.

1. Dye Carrier

Virtually all of the biphenyl used in dye carriers is released from the dyeing plants, either in air emissions or in waste waters. Industry spokesmen estimate that less than 5% of the biphenyl is exhausted as vapor, so the large bulk is released in the waste waters. A discussion involving the environmental fate of this water-released biphenyl is presented in Section IX-B-1. The high estimate given in Table VIII-1 was obtained by arbitrarily assuming that only 50% of the released biphenyl was effectively treated or treated at all; the low estimate was obtained by assuming all of the biphenyl was treated with a 95% efficiency.

2. Fungicide

As described in Section V-A-2, the biphenyl used as fungicide is bound by solvents to either tissue paper or to paper pads. The biphenyl will

Table VIII-1. Estimated Environmental Releases of Biphenyl

Use*	Quantities of Biphenyl (SRC Estimations)					
	Current Annual Use, Production or Content ($X10^6$ lbs)	Current Annual Environmental Release Estimates ($X10^6$ lbs)		Estimated 1966-1975 Use, Production, or Content ($X10^6$ lbs)	Estimated 1966-1975 Environmental Release ($X10^6$ lbs)	
		High	Low		High	Low
Dye Carrier	50	25	3	250-300	125-150	15-18
Fungicide	0.6-0.8	0.6-0.8	0.3-0.4	20-30	20-30	10-15
Dowtherm® A	1.5	small*	-	10-15	small*	-
Creosote Oils	10	10	10	100	100	100
Petroleum	110	small*	-	1000	0.01	-
Naphthalene Feedstocks and Toluene Dealkylation By-Product, Unrefined	30-40	small*	-	200-300	small*	-
Coal Tar, excluding Creosote Oil Fractions	3-10	unknown	-	30-100	unknown	-
Automobile Exhaust	-	unknown	unknown	-	unknown	unknown

* See discussions in this section

eventually dissipate from the papers as air emissions, due to biphenyl's volatility, if left open to the atmosphere. The high estimate given in Table VIII-1 was obtained by assuming all of the biphenyl was allowed to dissipate; the low estimate by assumming one-half of the papers were destroyed by incineration, thereby destroying the biphenyl.

3. Dowtherm® A

It would seem unlikely that large amounts of Dowtherm® A are released to the environment because decomposed or impure Dowtherm can be used for fuel purposes or purified via distillation.

There is no set "working-life" for Dowtherm® A (Anderson, 1976). As long as decomposition does not occur, the fluid can be used for many years (decomposition is dependent upon working temperature). In actual practice, the impurities are periodically removed from the system and the system is simply "topped-off" with fresh Dowtherm.

Because Dowtherm® A can last for years, the quantities in current use must be quite high. SRC estimates that 5.5 million pounds of Dowtherm® A were produced in 1975. It is possible that 30-40 million pounds or more are currently being used. An attempt to produce an exact figure for current use was unsuccessful.

4. Creosote Oils

As explained in Section VII-A-3, due to the nature of the use of creosote oils, any biphenyl content will be exposed to the environment through use. Due to biphenyl's volatility, this biphenyl will be exposed to the air as vapor emissions or may be leached by water from the treated wood.

5. Petroleum

It would seem unlikely that any large quantities of the very low percentage of biphenyl present in petroleum will be exposed to the environment. In Section VI-A-1, it was estimated that approximately 1000 pounds of biphenyl are exposed to the environment annually from oil spills. For the ten-year period between 1966-1975, a figure of 10,000 pounds was assumed for release determination.

6. Naphthalene Feedstock and Toluene Dealkylation By-Product, Unrefined

As for petroleum, it would seem unlikely that any large quantities of biphenyl present in these sources will be exposed to the environment. The biphenyl from these sources will probably be added to fuel oils which are burned. The biphenyl that is burned for fuel should be destroyed and, therefore, not released to the environment.

7. Coal-Tar, Excluding Creosote Oils

As explained in Section VII-A-3, the eventual fate of this product is not certain; therefore, no estimate is made.

8. Automobile Exhaust

See discussion of Section VII-A-4.

B. Diphenyl Oxide

Table VIII-2 lists the estimated environmental releases of diphenyl oxide. Explanations of estimates are given below.

1. Dye Carrier

All of the diphenyl oxide used in dye carriers is released from the dyeing plants, either in air emissions or in waste waters as previously

Table VIII-2. Estimated Environmental Releases of Diphenyl Oxide

Use*	Quantities of Diphenyl Oxide (SRC Estimation)					
	Current Annual Use ($X10^6$ lbs)	Current Annual Environmental Release Estimates ($X10^6$ lbs)		Estimated 1966-1975 Use ($X10^6$ lbs)	Estimated 1966-1975 Environmental Release ($X10^6$ lbs)	
		High	Low		High	Low
Dye Carrier	0.25	0.13	.013	1.0	0.5	0.05
Perfume and Soap	0.10	0.10	0.05	1.0-2.0	1.0-2.0	0.5-1.0
Dowtherm® A	4.0	small*	-	30-40	small*	-

* See discussion in this section

described for biphenyl dye carriers. The high estimate given in Table VIII-2 was obtained by assuming that only 50% of the released diphenyl oxide was effectively treated or treated at all; the low estimate was obtained by assuming all of the diphenyl oxide was treated with a 95% efficiency.

2. Perfumes and Soaps

It can be assumed that all of the diphenyl oxide used in perfumes and soaps will be released to the environment. The high estimate given in Table VIII-2 assumes no treatment at waste water facilities to degrade diphenyl oxide content; the low estimate assumes that 50% of the released diphenyl oxide is treated effectively.

3. Dowtherm® A

See discussion in Section VIII-A-3.

IX. Environmental Perspectives

A. Occupational Exposure to Man

The following OSHA standards have been established for exposure to biphenyl and diphenyl oxide in air:

Biphenyl	0.2 ppm (approximately 1 mg/m^3) (time weighted average)
Diphenyl Oxide	1.0 ppm (time weighted average)

There are no OSHA recommendations to control direct contact of biphenyl or diphenyl oxide in solid or liquid form; possible skin absorption of these substances is apparently not considered to have measureable health significance.

The following toxicity data are available for the two chemicals (Christensen and Luginbyhl, 1975; Opdyke, 1974; Haas et al., 1975; Branson, 1977):

Biphenyl:	inhalation - human	*TD_{Lo}: 4400 $\mu g/m^3$
	oral - rat	LD_{50}: 3280 mg/kg
	oral - rabbit	LD_{50}: 2400 mg/kg
	skin - rabbit	LD_{50}: 2500 mg/kg
	fish - fathead minnow	TL_m (96 hrs): 1.5 mg/l
	- fathead minnow	LC_{50} (96 hrs): 5.3 mg/l
Diphenyl Oxide:	oral - rat	LD_{50}: 3370 mg/kg
	skin - rabbit	LD_{50}: > 5000 mg/kg
	fish - fathead minnow	LC_{50} (96 hrs): 5.5 mg/l

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*Key to Abbreviations

TD_{Lo} - lowest published toxic dose
LD_{50} - lethal dose 50 percent kill
TL_m - tolerance median
LC_{50} - lethal concentration 50 percent kill

B. Release to the Environment

1. Biphenyl

Most of the biphenyl released to the environment by man is released by the textile dyeing industry. The larger dyers (Burlington, for example) operate mills which have their own waste treatment facilities to process wastes while most other dyers apparently release wastes to city or county facilities.

a. Effectiveness of Biphenyl Waste Treatment

The exact effectiveness of treatment of biphenyl wastes by each treatment plant cannot be ascertained because the individual treatment plants do not monitor biphenyl levels. Instead, they monitor BOD and/or COD levels.

To provide an example of COD levels before and after treatment, SRC contacted the largest Burlington Industries' mill, which is located in Greensboro, NC. Burlington operates their own waste treatment facility at this mill. Mr. Joe Ameen, Sanitary Engineer for the mill, reports that COD normally measures 1200-1500 mg/l on the influent stream to waste treatment while the effluent normally measures 200-300 mg/l. The effluent is discharged into a river. In addition to biphenyl, the influent stream contains other dye carriers, such as trichlorobenzene, butyl benzoate, etc., dyestuffs, emulsifiers, and all other factory wastes. Mr. Ameen also reports that in community waste treatment plants operated by Burlington in other cities, a 15% or more addition of community solid wastes to the Burlington wastes reduces COD levels of the effluent to 50-100 mg/l.

Dr. Peter Gaffney of the Biology Department of Georgia State University has been studying biphenyl problems in water at municipal

waste treatments for several years. He states (Gaffney, 1976) that biphenyl is effectively processed by the treatment plants; however, his concern has been directed at potential PCB formation during chlorine pre-treatments. This PCB formation is discussed in more detail in Section IX-B-1-c.

Biphenyl has been detected in river water by Webb et al. (1973) and Hites (1973). Hites identified biphenyl, trichlorobenzene, and butyl benzoate in the waters of the Merrimack River at 0.1-0.5 ppb concentration. Hites attributes the presence of these organics to upstream textile factories.

Also, W.C. Tichner of the Environmental Resources Center of Georgia Institute of Technology has been studying the problem of biphenyl effluents from polyester carpet manufacturing in Georgia. Tincher has measured biphenyl concentrations in streams at the point of effluent discharge to several miles downstream. He has found that the biphenyl concentration drops quite rapidly after effluent discharge. He attributes this phenomenon to the volatility of biphenyl (Tincher, 1976). It is worth noting that rather than complete biphenyl degradation, at waste treatment plants, or complete volatilization occurring, various degradation intermediates may be present (usually not determined) such as, phenylphenol (Gaffney, 1977 a). There has apparently been no work done showing the kinetics of biphenyl degradation completely to carbon dioxide and water; this would be desireable.

In 1974, the Sun Oil Co. commissioned Dr. J. Ferguson of Johns Hopkins University to experimentally determine biodegradation rates for biphenyl and other common dye carriers. To determine aerobic biodegradation

rates, typical treatment cultures were obtained and pre-conditioned to the dye carriers. All cultures received an initial dye concentration of 50 ppm. Extractions of the culture and the water system were made at various times and analyzed.

Figure IX-1 shows how long the microorganisms took to reduce the concentration of the dye carrier containing 95% biphenyl and of the other dye carriers (Haas et al., 1975). The biphenyl was totally biodegraded in about 48 hours.

b. Environmental Chlorination of Biphenyl

Dr. Peter Gaffney first reported finding PCB's in a sewage treatment plant's trickling filter bed in 1974 (Gaffney, 1974). He suggested that the PCB's were generated as a result of a high biphenyl influx from a textile mill coupled with a waste water pre-chlorination for odor control and disinfection. It was determined later, however, that commercial PCB's were entering this waste treatment facility. In laboratory tests, Gaffney found that PCB's were formed when 10 mg/l of biphenyl were added to dionized water held at 20°C, and then 1 mg/l of chlorine was added and the reactants kept in contact for one hour (Versar, 1976).

Carlson et al. (1975) conducted a detailed laboratory analysis to determine chlorine incorporation into biphenyl and other aromatic compounds under conditions utilized for water renovation. Table IX-1 is a summary of PCB and chlorobiphenyl formation under the various aqueous conditions used (Carlson et al., 1975). The results shown in Table IX-1 confirm the possibility of chlorine incorporation into the biphenyl nucleus under a variety of conditions.

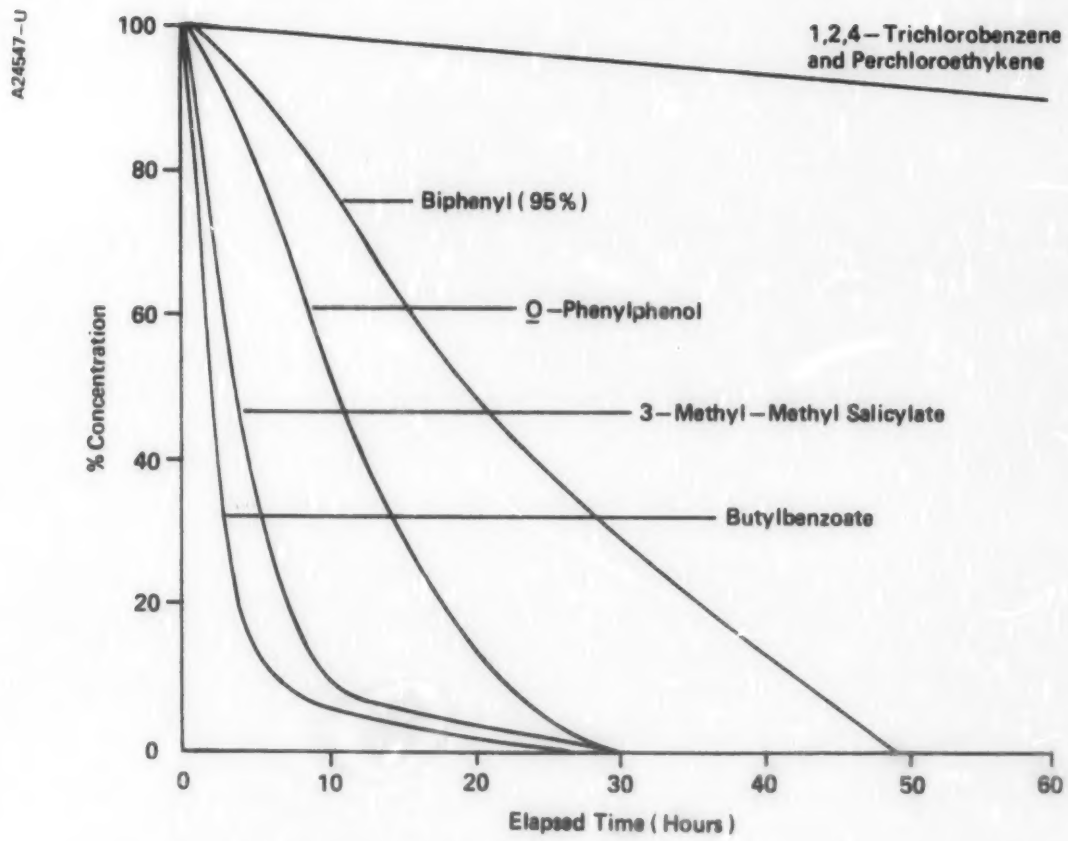


Figure IX-1. Reduction of Concentration Owing to Biodegradation - Analysis of Culture Cells and Water (Haas et al., 1975)

Table IX-1. Chlorination of Biphenyl Utilizing Water Renovation Conditions (Carlson et al., 1975)

Chlorine Source	pH	Chlorine, ppm	Reaction Time, hr	Reaction, %	Ppb of Chlorinated Product				
					2-	3-,4-	2,2'	2,3'-2,4'	4,4'-
$Ca(OCl)_2$	5.5	100	24	0.4	15	10			
$Ca(OCl)_2$	5.5	100	48	1.0	32	27			
$Ca(OCl)_2$	5.5	100	72	1.7	56	47			
$Ca(OCl)_2$	5.5	100	120	2.5	69	82			
$Ca(OCl)_2$	5.5	10	120	0.004	0.1	0.12			
$Ca(OCl)_2$	5.5	20	120	0.02	0.44	0.51			
$Ca(OCl)_2$	5.5	35	120	0.04	1.4	1.2			
$Ca(OCl)_2$	5.5	50	120	0.15	4.0	4.9			
$Ca(OCl)_2$	5.5	100	120	0.27	8.8	7.4			
Cl_2	2.1	10.9	0.25	2.2	120	10			20
NaOCl	2.8	295	0.25	9.3	450	190	10	130	40
Cl_2	4.9	266	0.25	0.1	5-10				
NaOCl	10.4	830	0.25	0.6	40				
Cl_2[a]	2.2	1350	0.25	16	180	80	80	370	500
NaOCl	7.0	2950	0.25	5.2	280	110		80	10

Saturated biphenyl solution found experimentally to be 6.0 mg/l.

[a]Higher chlorinated isomers also present.

Dr. Gaffney has conducted an investigation to determine if chlorobiphenyls can be produced in wastewater treatment plants because of the use of chlorine with municipal wastes containing biphenyl (Gaffney, 1977 b). The results indicated that various chlorobiphenyl isomers are produced during final chlorination. The chlorobiphenyl isomers predominately formed are the 2-chloro, 2,2'-dichloro, and 2,4'-dichloro isomers. A relatively small amount of trichlorobiphenyl was also detected. It should be noted that the term PCB should be reserved for only those biphenyl molecules having three or more chlorine atoms attached. Laboratory chlorination of influent and effluent from a municipal waste treatment facility also results in the formation of these and other chloro-organic substances (Gaffney, 1977 b).

Dr. Richard Johnsen has also conducted laboratory studies of biphenyl chlorination under conditions which may exist at waste treatment plants (Johnsen, 1975). Biphenyl in water (5 ppm) was added to chlorinated water given chlorine concentrations of 8, 83, and 830 ppm. Under ambient conditions and after aging for 24 hours and 1 week, the samples were analyzed, along with suitable controls, by gas chromatography. The results were somewhat surprising; when chromatographs of biphenyl reacted with Cl_2-water (83 ppm and 830 ppm) for 1 day are superimposed over a chromatograph of Arochlor 1221 (a commercial PCB), striking overlaps are observable, although peak heights are not the same. This preliminary work by Dr. Johnsen is being continued.

Dr. E.L. Kothny has suggested an interesting source of PCB and other chlorinated organics found in the environment (Kothny, 1976). He has proposed that the chlorine released from sea salt particles might chlorinate organics such as biphenyl found in the atmosphere. There is, however, no evidence to support this contention at present.

2. Diphenyl Oxide

The information and data given below have been acquired from the Dow Chemical Co. (Otis, 1976).

a. Effectiveness of Waste Treatment

"Generally, organic chemicals with a BOD_5 (5 day biochemical oxygen demand) value in excess of 60 percent of the stoichiometrically required amount of oxygen are readily degraded in conventional waste treatment facilities. Under favorable waste treatment conditions, concentrations of diphenyl oxide in waste streams have been reduced up to 95%. This magnitude of reduction is typical of that encountered with municipal wastes. Analytical methods are available for measuring the concentrations of diphenyl oxide in waters and waste streams. In the event of a gross discharge of diphenyl oxide into a river, techniques are available that can predict the downstream concentrations of diphenyl oxide based on some known rates and routes of removal from the river. These routes include microbial degradation (by a variety of aquatic microorganisms), absorption on suspended solids, and volatility from water" (Dow Technical Data Sheet - XAS-1075L).

b. Biodegradation

"The most desirable environmental property of diphenyl oxide is its ability to biodegrade into carbon dioxide and water in the presence of naturally occurring microorganisms. This observation is supported by a variety of tests including the standard biochemical oxygen demand (BOD) test, an oxygen probe test, and tests which measure the chemical disappearance from soil and river sediments. A postulated mechanism of diphenyl oxide conversion to carbon dioxide and water under the influence of aerobic microorganisms is believed to

involve some catechol-like intermediates. However, positive proof for this mechanism has proven difficult because of the transient existence of the intermediate compounds" (Dow Technical Data Sheet - XAS-1075L).

c. Bioconcentration

"Detection of chemical residues in fish has been the key environmental alert for DDT and PCB's. Consequently, the potential of diphenyl oxide to bioconcentrate was determined.* Bioconcentration is a measure of the relative distribution of a test chemical between fish tissue and exposure water. Diphenyl oxide has been found to bioconcentrate to only a limited extent, quite unlike DDT or PCB's. When placed in fresh water, the fish were found to eliminate diphenyl oxide rapidly, 50% each day compared to 50% each 30 days for an isomer of PCB's. These results show that hazardous or persistent concentrations of diphenyl oxide in fish are unlikely to occur" (Dow Technical Data Sheet - XAS-1075L).

The potential for biphenyl to bioconcentrate was also determined by Dow Chemical. Neely et al., (1974) determined the bioconcentration as the ratio of the uptake rate of the exposure chemical to the clearance rate. For biphenyl, the bioconcentration was found to be 438±48 while for diphenyl oxide the bioconcentration was 196±39.

---

*Results published by Neely et al., (1974). The log bioconcentration factor was experimentally determined as 2.29 (therefore, bioconcentration factor = 196).

X. Environmental Assessment

A. Biphenyl

Biphenyl is being released to the environment in quantities which may total 60 million pounds annually and perhaps even higher (SRC estimate). The largest known source of biphenyl release is from biphenyl's use as a dye carrier in the dyeing industry. Approximately 50 million pounds of biphenyl are annually used for dyeing applications (SRC estimate). This biphenyl is usually released in the wastewaters from the dyeing factories to either municipal treatment facilities or to on-site treatment facilities. Common forms of waste treatment appear to be successful in the processing of biphenyl wastes (Gaffney, 1976). Laboratory experiments have shown that typical c. tures from water renovation facilities are able to reduce biphenyl concentrations to nearly zero in only 48 hours (Haas et al., 1975). However, since biphenyl is not monitored at treatment facilities, the efficiency of general treatment cannot be determined with certainty. Also, the method of treatment may be a significant factor in the amount of biphenyl converted by biodegradation. Tincher (1976) has found that the concentration of biphenyl released to streams rapidly falls below 1 ppm after release, due to biphenyl's volatility. This suggests that methods which allow biphenyl wastes to be exposed to the atmosphere for periods of time during treatment may allow quantities of biphenyl to be released into the air by volatilization.

A major concern of biphenyl release to waste treatment plants from the dyeing industry is the evidence which indicates that biphenyl-containing sewage may be chlorinated to PCB or chlorobiphenyl isomers during pre-chlorination processes for disinfection and deodorization (Gaffney, 1974, 1976, 1977b;

Carlsen, 1975; Johnsen, 1975). Laboratory experiments which have mimicked treatment facility methods have found that the biphenyl nucleus can be chlorinated with four, or usually less, chlorine atoms. Commercially prepared PCB's have a much greater degree of chlorination and have certainly less biodegradability than the PCB and chlorobiphenyl isomers which may be generated at waste treatment plants. Although sufficient research has yet to be done for conclusive results, the present indications suggest that chlorination of biphenyl-containing sewage deserves a great deal of consideration and perhaps restriction.

Another major source of biphenyl release to the environment is from creosote oils which are used to preserve wood, especially railroad ties and telephone poles. Biphenyl is present in creosote oils because it is one of the constituents in the high-boiling fractions of coal tar from which these creosote oils are derived. It is likely that nearly 10 million pounds of biphenyl are annually released to the atmosphere by biphenyl's volatilization or to water by leaching from creosote oils (SRC estimate).

An uncertain but potentially significant source of biphenyl exposure to the atmosphere is automobile exhaust. It is possible that biphenyl is one of the many hydrocarbons present in auto emissions; however, there is no available monitoring data to confirm this supposition. Even if biphenyl is present in only a very small fraction of a percent, the annual quantity emitted could be very large due to the enormous amounts of hydrocarbons emitted by autos.

B. Diphenyl Oxide

Diphenyl oxide is being released to the environment in quantities which may total 0.25 million pounds annually (SRC estimation). The two major sources

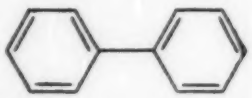
of diphenyl oxide release are soap and perfume use and dye carrier use. Man has been exposed to diphenyl oxide as an ingredient in some soaps and perfumes since the early 1930's. Laboratory and practical experience have suggested no adverse effects from diphenyl oxide use via perfumes and soaps. The Council of Europe (1970) included diphenyl oxide in the list of temporarily admissible artificial flavouring substances (Opdyke, 1974); however, spokesmen for Dow Chemical (Branson, 1977) indicate that flavouring should mean odor and not food additive. They question the use of diphenyl oxide as a food additive without more data.

Industrial effluents from plants using diphenyl oxide as a dye carrier can apparently be effectively treated in conventional waste treatment facilities (Dow Technical Literature - XAS-4169L) when such treatment is used.

Appendix A

Physical Properties

Biphenyl (Monsanto Tech. Bull. 1C/FF-29)

Melting point, °C	69	
Boiling point at 760 mm Hg, °C	255	Vapor pressure 0.0097 mm Hg at 25°C**
10.5 mm Hg, °C	118	
Specific gravity, 20°/4°C	1.04	
77°/4°C	0.99	
Lbs./gallon at 77°C	8.23	
Refractive index, n_D^{77}	1.588	
Viscosity at 70°C, Saybolt Sec.	31.2	
100°C, Saybolt Sec.	28.8	
Surface tension at 129,2°C, dynes/cm	39.5	
Flash point, closed cup, °C	113	
Open cup, °C	124	
Latent heat of fusion, Btu/lb.	53.1	
Specific heat, Btu/lb/°F	0.43	
Odor	Pleasant, peculiar	
Appearance	Colorless to pale yellow crystallized solid or flakes	
Molecular Weight	154.20	
Empirical Formula	$C_6H_5C_6H_5$	
Structural Formula		

Solubilities - Grams biphenyl per 100 cc of solvent

Solvents		Solubility	°C
Hydrocarbons	Mineral Spirits	16.9	26
	Gasoline (Texaco)	24.1	26
	Kerosene	17.5	27
	Benzene	81.5	27
	Xylene	56.9	27
	Turpentine	24.2	24
	Toluene	62.0	18
Water		0.00018*	
		0.00075 at 25°C**	

* 95% Biphenyl dye carrier (Haas et al., 1975)
** Branson (1977)

Diphenyl Oxide (Dow Form No. 110-288-72)

	DIPHENYL OXIDE GRADE		
	Technical	Perfume	Industrial
Molecular Weight	170.2	170.2	-
Boiling Point °C 760 mmHg	257°	257°	255°
Specific Gravity 25/25°C	1.070	1.070	1.065-1.075
Pound per gallon, 25°C	8.92	8.92	8.92
Refractive Index, 25°C	1.578	1.579	-
Freeze Point °C	26°	27°	15°
Flash Point °F COC	239°	239°	235°
Fire Point °F	258°	258°	255°
Auto Ignition Point °F	1144°	1144°	-
Latent Heat of Vaporization Cal/mole at B.P.	11,800	11,800	-
Approximate Solubility g/100g Solvent at 25°C			
Acetone	∞	∞	∞
Ether	∞	∞	∞
Benzene	∞	∞	∞
Methanol	∞	∞	∞
Water	20.8 ppm	21 ppm	21 ppm
Carbon tetra chloride	∞	∞	∞
n-Heptane	∞	∞	∞

Solubility of DPO in water at 25°C	20.8 ppm
Solubility of water in DPO at 25°C	0.071%
Solubility of water in DPO at 30°C	0.077%

BOILING POINTS OF DIPHENYL OXIDE

Boiling Point	MM Hg
257.9°C	760
181.3°C	100
147.1°C	30
121.0°C	10
77.0°C	1

Vapor pressure 0.019 mm Hg at 25°C*
*Branson (1977)

Appendix B

Material Safety Data Sheets

MATERIAL SAFETY DATA SHEET

(APPROVED BY THE U.S. DEPARTMENT OF LABOR AS - "essentially similar" to form OSHA-20)

Information on this form is furnished solely for the purpose of compliance with the Occupational Safety and Health Act of 1970 and shall not be used for any other purpose. Use or dissemination of all or any part of this information for any other purpose may result in a violation of law or constitute grounds for legal action.

Section 1 NAME & PRODUCT

MANUFACTURER'S NAME	CITY, STATE, ZIP CODE	EMERGENCY PHONE NO. - 24 HOURS
DOW CHEMICAL U.S.A.	MIDLAND, MICHIGAN 48640	517 - 636 - 4400

DATE THIS FORM WRITTEN	PREPARED BY (Signature)
February 19, 1973	C. F. Kimmel

TRADE NAME: Diphenyl Oxide, Technical — Diphenyl Ether

Section 2 INGREDIENTS

	%	TLV (units)
Diphenyl oxide	95	1 ppm
(Not a specification value)		

Section 3 PHYSICAL DATA

BOILING POINT (°F.)	498	SOLUBILITY IN WATER	Insoluble
VAPOR PRESSURE (mmHg at 20°c)	---	SPECIFIC GRAVITY (H_2O = 1)	1.070 @ 27/4°C.
VAPOR DENSITY (air = 1)	---	% VOLATILE BY VOLUME	---

APPEARANCE: Colorless liquid

Section 4 FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (AND METHOD USED)	FLAMMABLE LIMITS (STP IN AIR)	
205 °F Cleveland Open Cup	L.F.L. 0.8	U.F.L. 1.5

EXTINGUISHING MEDIA → [X] WATER FOG [X] FOAM [X] ALCOHOL FOAM [X] CO_2 [X] DRY CHEMICAL [ ] OTHER

SPECIAL FIRE FIGHTING PROTECTION EQUIPMENT AND HAZARDS

None.

Section 5 REACTIVITY DATA

STABILITY (NORMAL CONDITIONS)		CONDITIONS TO AVOID
[X] STABLE	[ ] UNSTABLE	

INCOMPATIBILITY — MATERIALS TO AVOID: [ ] WATER [ ] ACID [ ] BASE [ ] CORROSIVE [ ] OXIDIZING MATERIAL; OTHER [ ]

HAZARDOUS DECOMPOSITION PRODUCTS

None.

HAZARDOUS POLYMERIZATION			CONDITIONS TO AVOID
		MAY OCCUR	
	X	WILL NOT OCCUR	

Section 6 SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Small spills - absorb in sweeping compound.
Large spills - call Dow emergency number for instructions.

WASTE DISPOSAL METHOD

Burn or bury in accordance with local ordinances.

MATERIAL SAFETY DATA SHEET (CONT.)

DOW CHEMICAL U.S.A.
MIDLAND, MICHIGAN 48640

Section 7 HEALTH HAZARD DATA

Low single dose oral; LD_{50} 4000 mg/kg for both rats and guinea pigs. Estimating from these data, the lethal dose for a 100 pound person may be in the range of 3/4 cupful.

EYE CONTACT

Mild to moderate irritation; unlikely to cause injury.

SKIN CONTACT

Occasional contact - no adverse effects expected.
Mild to moderate irritation upon repeated, prolonged contact.

SKIN ABSORPTION

Not readily absorbed - No LD_{50} determined because of lack of indication of problem from absorption.

INHALATION

TLV: 1 ppm - based on odor control. No problem at room temperature.

EFFECTS OF OVEREXPOSURE

Disagreeable odor, possible liver injury at high concentration.

FIRST AID PROCEDURE

EYE FLUSH WITH FLOWING WATER	EYES & SKIN: Flush with plenty of water; get medical attention if irritation develops. Remove contaminated clothing and free of chemical before reuse. INHALATION: If discomfort develops from breathing vapors, get patient to fresh air. INGESTION: No known antidote; treat symptomatically.	NEVER GIVE FLUIDS OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS OR HAVING CONVULSIONS

Section 8 SPECIAL PROTECTION INFORMATION

VENTILATION

Sufficient to control to TLV.

RESPIRATORY PROTECTION (specify type)

When disagreeable odors occur, full-face mask and canister for organic vapors.

PROTECTIVE CLOTHING

Clean clothing.

EYE PROTECTION

☐ NOT NORMALLY NECESSARY ☒ SAFETY GLASSES WITHOUT SIDE SHIELDS ☐ SAFETY GLASSES WITH SIDE SHIELDS ☐ CHEMICAL WORKERS GOGGLES

☐ GAS TIGHT GOGGLES OR EQUIVALENT ☐ OTHER

Section 9 SPECIAL PRECAUTIONS OR OTHER COMMENTS

SPECIAL PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Use reasonable care. Store in cool, dry place.

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MATERIAL SAFETY DATA SHEET

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Section 1 NAME & PRODUCT

MFR'S OR SUPPLIER'S NAME	MFR'S OR SUPPLIER'S ADDRESS	EMERGENCY TELEPHONE NO.
DOW CHEMICAL U.S.A.	MIDLAND, MICHIGAN 48640	517 - 636 - 4400

DATE THIS FORM WAS PREPARED	SIGNATURE OF PREPARER (Signature)
February 16, 1976	C. E. Kennel

TRADE NAME

Biphenyl, High Purity

Section 2 INGREDIENTS

Biphenyl, minimum	99.3

Section 3 PHYSICAL DATA

BOILING POINT °F	491	SOLUBILITY IN WATER @ 25°C	0.0073 g/l
VAPOR PRESSURE (mmHg or 20°C)	---	SPECIFIC GRAVITY (H2O=1)	1.19 g/cm³ @25°C
VAPOR DENSITY (air=1)	---	% VOLATILE BY VOLUME	Not Applicable

APPEARANCE White solid; odor - moth balls

Section 4 FIRE AND EXPLOSION HAZARD DATA

FLASH POINT AND METHOD USED	FLAMMABLE LIMITS
233 °F Tag Closed Cup	LEL 0.6 @ 232°F UEL 5.8 @ 311°F

EXTINGUISHING MEDIA → [X] WATER FOG [X] FOAM [ ] ALCOHOL FOAM [X] CO2 [X] DRY CHEMICAL [ ]

SPECIAL FIRE FIGHTING PROTECTION EQUIPMENT AND HAZARDS

None

Section 5 REACTIVITY DATA

STABILITY (NORMAL CONDITIONS)	CONDITIONS TO AVOID
[X] STABLE [ ] UNSTABLE	

INCOMPATIBILITY						
[ ] WATER	[ ] ACID	[ ] BASE	[ ] CORROSIVE	[X] OXIDIZING MATERIAL	[ ] OTHER

HAZARDOUS DECOMPOSITION PRODUCTS

None

HAZARDOUS POLYMERIZATION		CONDITIONS TO AVOID
	MAY OCCUR	
X	WILL NOT OCCUR	

Section 6 SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Scoop up and salvage if possible.

WASTE DISPOSAL METHOD

Observe Federal, State and Local laws. Contact The Dow Chemical Company for disposal instructions.

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MATERIAL SAFETY DATA SHEET (CONT.

DOW CHEMICAL U.S.A.
MIDLAND, MICHIGAN 48640

Section 7 HEALTH HAZARD DATA

Low single dose oral toxicity. LD_{50} rats is greater than 4000 mg/kg. Estimating from these data, the lethal dose for a 100 lb. person may be 4-5 ounces.

Up to slight irritation but no corneal injury.

Short single exposure not likely to cause significant irritation. Prolonged or repeated exposure may cause slight irritation.

Not likely to be absorbed in toxic amounts.

TLV 0.2 ppm or 1 mg/m³ (1974)

Respiratory irritation.

FIRST AID PROCEDURES

EYE: EYES: Flush with plenty of water for 5 minutes and get medical help if ill effects occur. SKIN: Wash with soap and water. Remove grossly contaminated clothing and wash before reuse. INHALATION: If ill effects occur, get person to fresh air and get medical help. INGESTION: Not likely a problem. If large amounts are swallowed, see above, promptly induce vomiting and get medical help.*

NEVER GIVE FLUIDS OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS CONVULSING OR HAVING CONVULSIONS

Section 8 SPECIAL PROTECTION INFORMATION

Control dusts or mists to TLV.

Respiratory protection required in absence of proper environmental control. If required, use an approved dust respirator.

Clean body covering clothing.

EYE PROTECTION: [ ] [X] [ ] [ ] [ ] GAS TIGHT GOGGLES FOR VAPOR EXPOSURE [X] Eye fountain and washing facilities near work area.

Section 9 SPECIAL PRECAUTIONS OR OTHER COMMENTS

Practice reasonable care and cleanliness to avoid gross skin and eye contact. Avoid breathing vapors and dusts if generated.

*NOTE TO PHYSICIAN: No specific antidote known. Treatment depends on the sound judgment of the physician and the individual reactions of the patient.

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MATERIAL SAFETY DATA SHEET

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Section 1 NAME & PRODUCT

MANUFACTURER'S NAME	CITY, STATE, ZIP CODE	EMERGENCY PHONE NO. 24 HOURS
DOW CHEMICAL U.S.A.	MIDLAND, MICHIGAN 48640	517 - 636 - 4400

DATE PREPARED OR REVISED	PREPARED BY (Signature)
November 13, 1974	C. R. Swinnerton

TRADE NAME

DOWTHERM® A heat transfer fluid

Section 2 INGREDIENTS

	%	TLV
Diphenyl oxide	73.5	1ppm
Diphenyl	26.5	

(Not specification values)

Section 3 PHYSICAL DATA

BOILING POINT (°F.)	494.8	SOLUBILITY IN WATER	13.8ppm @ 60°F
VAPOR PRESSURE (mmHg at 20°C)	0	SPECIFIC GRAVITY (H_2O = 1)	1.050-1.075 @ 25/25
VAPOR DENSITY (air = 1)	>1	% VOLATILE BY VOLUME	---

APPEARANCE Straw-colored liquid, aromatic odor.

Section 4 FIRE AND EXPLOSION HAZARD DATA

FLASH POINT AND METHOD USED	FLAMMABLE LIMITS (STP IN AIR)	
255°F Cleveland Open Cup	L.F.L. 0.5% (500°F)	U.F.L. 6.2% (500°F)

EXTINGUISHING MEDIA → [X] WATER FOG [X] FOAM [ ] ALCOHOL FOAM [X] CO_2 [X] DRY CHEMICAL [ ] OTHER

SPECIAL FIRE FIGHTING PROTECTION EQUIPMENT AND HAZARDS

Self-contained breathing apparatus may be needed in enclosed spaces.

Section 5 REACTIVITY DATA

STABILITY (NORMAL CONDITIONS)		CONDITIONS TO AVOID
[ ] STABLE	[ ] UNSTABLE	

INCOMPATIBILITY (MATERIALS TO AVOID): [ ] WATER [ ] ACID [ ] BASE [ ] CORROSIVE [X] OXIDIZING MATERIAL [ ] OTHER

HAZARDOUS DECOMPOSITION PRODUCTS

None

HAZARDOUS POLYMERIZATION		CONDITIONS TO AVOID
	MAY OCCUR	
X	WILL NOT OCCUR	

Section 6 SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

Soak up with absorbant material.

WASTE DISPOSAL METHOD

Incineration in approved equipment.

OSHA Form 1

DOWTHERM® A

MATERIAL SAFETY DATA SHEET (CONT.)

DOW CHEMICAL U.S.A.
MIDLAND, MICHIGAN 48640

Section 7 HEALTH HAZARD DATA

Low single dose oral toxicity. LD_{50} rats is in the range of 2000 to 4000 mg/kg. Estimating from these data, the lethal dose for a 100 lb. person may be 2 to 4 fluid ounces.

EFFECTS OF CONTACT

Up to mild irritation but no corneal injury.

EFFECTS OF SHORT TERM EXPOSURE

Short single exposure not likely to cause significant irritation. Prolonged or repeated exposure may cause up to mild irritation.

ABSORPTION Not likely to be absorbed in toxic amounts. Very low in toxicity by this route.

TLV 1ppm (1973)

EFFECTS OF OVEREXPOSURE

Inhalation - vapors have a disagreeable odor.

FIRST AID DUE TO EYE CONTACT: FLUSH WITH FLOWING WATER AT LEAST 5 MINUTES

EYES: Flush with plenty of water for 5 minutes and get medical help if ill effects occur. SKIN: Promptly flush skin with plenty of water. Remove badly contaminated clothing and wash before reuse. INHALATION: Not likely a problem due to disagreeable odor. If ill effects occur, get person to fresh air and get medical help. INGESTION: Not likely a problem. If large amounts are swallowed, see above, promptly induce vomiting and get medical help.*

NEVER GIVE FLUID OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS OR HAVING CONVULSIONS

Section 8 SPECIAL PROTECTION INFORMATION

VENTILATION Good room ventilation usually adequate for most operations. Control vapors to TLV.

RESPIRATORY PROTECTION Specify type

None likely to be needed. For emergencies of ½ hour or less, full face mask plus an organic vapor canister.

PROTECTIVE CLOTHING

Clean body covering clothing.

EYE PROTECTION

☐ NOT NORMALLY NECESSARY ☒ SAFETY GLASSES WITHOUT SIDE SHIELDS ☐ SAFETY GLASSES WITH SIDE SHIELDS ☐ CHEMICAL WORKER'S GOGGLES

☐ GAS TIGHT GOGGLES OR EQUIVALENT ☐ OTHER

Section 9 SPECIAL PRECAUTIONS OR OTHER COMMENTS

SPECIAL PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Practice reasonable care and caution. Avoid breathing vapors if generated. Avoid direct contamination of water because of fish toxicity.

NOTE TO PHYSICIAN: No specific antidote known. Treatment depends on the sound judgment of the physician and the individual reactions of the patient.

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